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THE DIFFUSION OF WATER VAPOUR THROUGH VARIOUS BUILDING MATERIALS¹

By J. D. BABBITT

Abstract

A method of measuring the diffusion coefficient of water vapour through solids is outlined, and a table of the coefficients for various materials used in building construction is given. The method of employing these coefficients to calculate the vapour pressure gradient through a typical wall is shown, and this is applied to estimate the resistance to water vapour necessary to prevent condensation.

Introduction

The importance of a thorough knowledge of the cause and mechanism of moisture condensation in walls and roofs of buildings has become increasingly evident during the past few years through the report of numerous structural defects from this cause and also as a result of recent experimental work (6, 9). The experiments of Teesdale at the Forest Products Research Laboratory at Madison, Wisconsin, and those of Rowley at Minneapolis have shown conclusively that the condensation of moisture arises from the migration of water vapour from the warm interior of the building through the interior portions of the wall until it reaches a point in the wall where the temperature is below the dew-point. Here, condensation occurs, so that water and ice accumulate; this results directly in a loss in the insulation of the wall and indirectly in structural deterioration through dry rot, etc. The solution of this problem, as pointed out by both Teesdale and Rowley and subsequently by numerous other writers, lies in preventing the migration of the moisture from the warm side of the wall to the point of condensation; that is to say, the interior of the wall, which usually consists of plaster on some form of plaster base (with perhaps some added insulation either of wallboard type or in the nature of a fill), must be made so impervious to water vapour that there will never be an accumulation of sufficient water vapour within the wall to allow condensation. Since it is obvious that walls as present constructed do not offer sufficient resistance to the passage of water vapour, it is necessary to add some type of vapour barrier on the interior portion of the wall to prevent moisture movement. The three types of material which are, at present, advocated as vapour barriers are (cf. Teesdale):—

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1. Asphalt-impregnated and surface-coated sheathing paper, glossy surfaced, weighing 35 to 50 lb. per roll of 500 sq. ft.
2. Laminated sheathing paper made of two or more sheets of kraft paper cemented together with asphalt.
3. Double-faced reflective insulation mounted on paper.

These materials have been tested by both Teesdale and Rowley and there is no doubt that, when they are suitably applied, the vapour diffusion through them is so small that the possibility of the condensation of moisture under any circumstances is negligible.

To show that the use of some material impervious to water vapour on the interior part of the wall would stop all condensation was the first step towards the solution of this problem. But now it is essential to continue the investigation until the mechanism of moisture movement through buildings is as clearly understood as that of heat transfer. The following three factors affect the movement of moisture through any structure:

1. The temperature distribution through the wall. This, of course, is dependent on inside and outside temperatures and on the thermal resistance of the various parts of the wall.
2. The moisture content of the air on both the interior and exterior of the structure.
3. Resistance of the various parts of the wall to vapour movement.

It is essential to point out that in the calculation of the possibility of condensation in a wall the permeability of the exterior portions of the wall plays a role only a little less important than that of the interior portions. The important point is that the moisture should escape through the exterior portions of the wall more quickly than it enters the interior portions, as then there will be no possibility of an accumulation of sufficient moisture for condensation. Therefore, an alternative method of preventing moisture is to make the exterior portion of the wall extremely pervious to moisture by leaving holes or cracks to the outside. This method, however, is not desirable, as it allows water in the form of rain to enter the wall. Hence the established method of preventing condensation is to make the interior so impervious to moisture that the exterior can be made wind and rain proof without any possibility of condensation.

When the three factors listed above are known it is possible to calculate accurately the distribution of moisture through a wall under equilibrium conditions. Since the temperature distribution can be determined from a knowledge of the inside and outside temperatures and the thermal conductivities of the materials constituting the wall, a table of dew-points is sufficient to show the probability of condensation, once the moisture distribution through the wall has been obtained. An indication of this procedure has been presented by Miller (5). Unfortunately, however, the resistance of various building materials to water vapour is very imperfectly known. Some work has been done on various packaging materials, and

this has been summarized by Carson (2); there are some excellent measurements on paints (3, 10); a few measurements on wood (4, 7); and some miscellaneous measurements given by Miller (5); but there are no generally accepted data for the great mass of material used for constructional purposes.

In this paper the results of some measurements made at the National Research Laboratories, Ottawa, will be presented, and some indication given of their application to diffusion problems.

Explanation of Diffusion Coefficient

In a preliminary paper (1) the significance of the diffusion coefficient and the method by which it is measured were explained; these points will therefore be outlined only briefly here. To treat the transfer of water vapour as a diffusion phenomenon is a somewhat questionable procedure, as there is undoubted evidence that the phenomenon of water vapour transfer is a more complicated process than simple diffusion. Almost all materials that are used for building purposes are hygroscopic, *i.e.*, they absorb a definite weight of water if exposed to an atmosphere of a definite relative humidity. The relation between the amount of moisture absorbed and the relative humidity is different for different materials, and in no case is a simple linear relation obtained. It has been quite definitely established that in the movement of moisture through hygroscopic materials a much more intimate relation exists between the water and the material than in pure diffusion. This is strikingly emphasized by the fact that there is no connection between the permeability of a substance to air, which is a case of pure diffusion, and its permeability to water vapour. Rubber has been shown to be 50 times more permeable to water vapour than to hydrogen, and since lighter gases diffuse much more rapidly than heavier ones there must be some additional action in the case of water. However, it is not the intention to deal with the mechanism of water vapour transfer in this paper, but rather to present some measurements of the rate of transfer and to show how these may be applied to practical cases.

In order to obtain a working basis for the treatment of moisture transfer it is essential, notwithstanding the remarks above, to treat the transfer of vapour as a diffusion phenomenon and to make use of the various relations that have been found to hold for such phenomena. In fact, the errors introduced by the use of this assumption are, for all conditions that exist in practice, much smaller than errors introduced by other unavoidable factors, such as variations in materials, methods of construction, etc. It is only when high humidities (greater than 80% relative humidity) occur that the departure from the laws of diffusion becomes of sufficient magnitude to influence the results unduly (2, 8, 3).

In this paper, therefore, the work will be presented as based on the assumption that the transfer of moisture is a diffusion process and as such obeys Fick's law. For this purpose the law is used in the following form:

$$W = \frac{dAt}{X} (P_1 - P_2),$$

where W is the weight of water vapour diffusing in time t through a material of thickness X and area A when the vapour pressures on the two sides of the material are P_1 and P_2 respectively. The quantity d is the coefficient of diffusion or the diffusivity. It may be defined as the amount of water vapour passing through unit area of the material in unit time when unit vapour pressure difference is maintained per unit thickness. In the treatment of non-homogeneous materials it is advantageous to consider the diffusance $D = \frac{d}{X}$ instead of the diffusivity. To facilitate the calculation of the diffusion through composite structures, the concept of the resistivity and resistance, the reciprocals of the diffusivity and the diffusance respectively, are convenient.

Fick's law is similar in form to Fourier's equation for the transfer of heat, so that once the assumption is made that Fick's law does satisfactorily explain water vapour diffusion then all the mathematical analysis that has been developed for thermal applications becomes available. The calculation of the humidity gradient through a wall is then similar in method to the determination of temperature gradient through the wall.

Experimental

The Measurement of the Diffusion Coefficient.

On the assumption that the transfer of water vapour through a solid material obeys Fick's law, it is a simple matter to evaluate the coefficient d . It is necessary only to determine the weight of moisture that passes through a sample of the material per hour when different constant relative humidities are maintained on the two sides of the sample.

In this investigation the diffusion coefficient has been measured by an application of the cell method: that is to say, the material, the coefficient of which is to be measured, is placed over the top of the dish or cell so as to completely shut off the interior of the cell from the external atmosphere. The cell is filled with calcium chloride, an aqueous solution of sulphuric acid, or some other desiccant, so as to give the desired vapour pressure within the cell. The whole arrangement (cell plus sample) is then placed in an enclosure maintained at a constant temperature and humidity. The gain in weight of the cell, after equilibrium has been attained, is then equal to the weight of water diffusing through the specimen. Two types of cells used in this research are shown in Figs. 1 and 2. The first, Fig. 1, used for thick samples, consists of a straight-walled glass vessel similar to a crystallizing dish, and the specimen is placed flush with the upper edge of the vessel. The edges of the specimen are covered with a layer of wax before being placed in the cell so as to prevent any possibility of edge loss, and after it has been inserted in the dish the space between the edge of the sample and the wall of the vessel is sealed with wax. The second, Fig. 2, is constructed from duralumin and is so made that samples of any thickness up to 1 in. may be tested. The sample rests on a horizontal rim and is firmly pressed against this by a screw cap. This surface is first coated with wax and heated to receive the

specimen. If the thickness of the sample is comparable to the width of the rim the edges of the sample must also be sealed with wax. The area of the duralumin cells used was about 45 sq. cm., and that of the glass vessels, about 70 sq. cm.

In accordance with the suggestion made by Carson (2), a solid desiccant (calcium chloride) was used in the cells, and these were so filled that the surface of the desiccant was almost touching the lower surface of the specimen. In this way, the air space between the desiccant and the lower surface of the sample was made as small as possible, so that the error introduced by assuming that the vapour pressure at the lower surface of the sample was equal to that of the desiccant was negligible.

The arrangement of the apparatus in the constant humidity chamber is shown in Fig. 3. This chamber had the internal dimensions 1 ft. by 2 ft. by 2 ft. and was constructed of five-ply wood, which was painted on the inside with three coats of aluminium paint. A small fan with 8-in. blades was so placed as to blow a stream of air across the surface of a flat tray containing a saturated aqueous solution, and from this on to the measuring cells. In this way the air in contact with the upper surface of the samples was kept at a humidity corresponding to that of the solution. The temperature within the chamber was kept constant by means of a thermostat controlling a 100 watt lamp. The temperature and relative humidity were recorded on a recording humido-graph. This arrangement is slightly different from that described in a previous paper (1), but it was found essential to

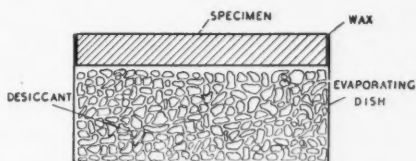


FIG. 1. Cell used for thick samples.

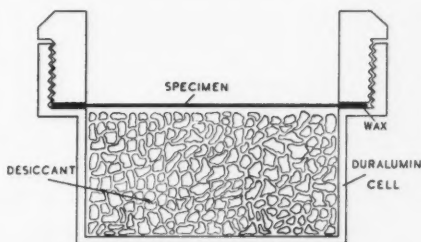


FIG. 2. Cell used for samples of any thickness up to 1 in.

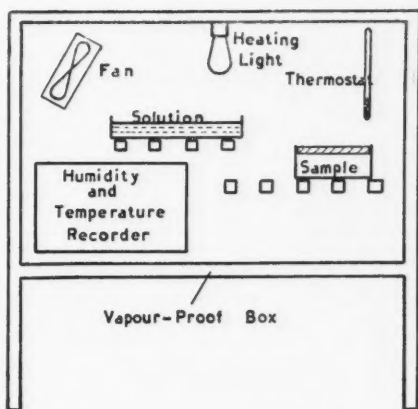


FIG. 3. Arrangement of apparatus in humidity chamber.

place the tray containing the solution directly between the fan and the samples in order to obtain the correct humidity conditions.

In most of the experiments reported here the temperature of the box was held constant at a temperature in the vicinity of 90° F. This temperature was chosen mainly for convenience; most of the measurements were taken during the summer months when it would have been impossible to maintain a lower temperature without some method of cooling. As it has been found by a number of investigators (cf. Carson (2)) that, except for high temperatures or humidities, the rate of transpiration of moisture is governed by the vapour pressure difference irrespective of the temperature, the error introduced by transposing the measured coefficients to room temperatures is not great. The humidity in the chamber was maintained constant by means of a saturated sodium chloride solution. According to the International Critical Tables this corresponds to a relative humidity of 75% at 91° F. The humidity was checked as closely as possible by means of a small piece of fibreboard which was left exposed to the atmosphere in the chamber. The moisture absorption curve for this material had previously been determined, so that the increase of weight of the fibreboard when left in the chamber enabled the humidity to be roughly checked. It was found, within the errors of the experiment, to be 75% relative humidity.

In the determination of the vapour transmissions the cells were weighed every 24 hr. The increase in weight was then plotted against the time. When a straight line was obtained the slope was measured; this gave the vapour transmission per hour. Since most of the materials were hygroscopic, a considerable time was required before the material was in equilibrium with the moisture in the atmosphere. During this time the weight of the cell increased either more quickly or more slowly than under equilibrium conditions, the rate depending on whether the sample was dry or damp when placed in the cell. A typical curve for a sample composed of five pieces of Presdwood is shown in Fig. 4. This sample was dry when placed in the apparatus; considerable time was therefore required before equilibrium was attained. In the case of thin materials or non-hygroscopic material, equilibrium is attained

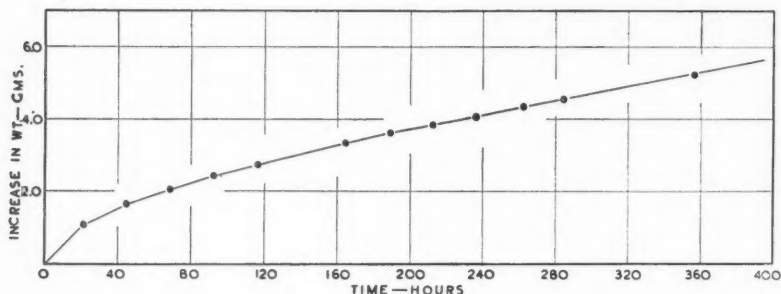


FIG. 4. Showing how the weight of a sample consisting of five thicknesses of Presdwood varies with time.

almost immediately, so that the final linear curve relating increase of weight with time passes through the origin.

Discussion of Results

The diffusion coefficients obtained by the above method are given in Table I. In cases of those non-homogeneous materials where the impedance to moisture is obtained mostly from a special part of the material (*e.g.*, a surface layer) and is not proportional to the thickness, the diffusance, D , is given instead of the diffusivity, d . The units used are grams per 24 hr. per sq. meter per vapour pressure difference of 1 mm. of mercury per cm. in the case of d , and grams per 24 hr. per sq. meter per vapour pressure difference of 1 mm. of mercury across the material in the case of D .

TABLE I
DIFFUSION COEFFICIENTS

Temperature = 91.0° F.

External vapour pressure = 27.2 mm. of Hg. = 75% relative humidity

Internal vapour pressure = 0.0 mm. of Hg.

Material	Thickness cm.	Diffusance D gm./24 hr./ sq.m./mm. Hg.	Diffusivity d gm./24 hr./ sq.m./ mm.Hg. cm.
Fibreboard	1.25	19.7	24.8
Fibreboard; asphalt on one surface; applied by rolling	1.25	2.6	
Fibreboard; a glossy coating of asphalt on one surface; applied by dipping	1.6	5.6	
Fibreboard, laminated; two $\frac{1}{2}$ in. samples cemented together with asphalt	2.5	0.89	
Fibreboard, laminated; 6 layers of fibreboard with 5 layers of asphalt	1.34	0.075	
Fibreboard	2.69	12.0	32.2
Fibreboard (above sample reduced in thickness)	2.04	14.1	28.7
Fibreboard (above sample reduced in thickness)	1.52	18.3	27.8
Fibreboard (above sample reduced in thickness)	1.03	24.2	24.8
Fibreboard (above sample reduced in thickness)	0.51	43.3	22.2
Wood (Spruce)	1.43	1.13	1.62
Wood (Spruce)	1.22	1.31	1.60
Wood (Spruce)	1.03	1.28	1.32
Wood (Spruce)	0.82	1.60	1.31
Wood (Spruce)	0.59	2.35	1.39
Wood (Spruce)	0.41	3.36	1.37
Wood (Pine)	2.03	0.61	1.25
Wood (Pine)	1.64	0.82	1.34
Wood (Pine)	1.26	1.12	1.41
Wood (Pine)	0.80	1.80	1.43
Wood (Pine)	0.43	3.13	1.34
Wood (Pine) A	1.29	2.10	2.71
Wood (Pine) A 1 coat aluminium paint		1.11	
Wood (Pine) A 2 coats aluminium paint		0.30	
Wood (Pine) A 3 coats aluminium paint		0.23	

TABLE I—*Concluded*
 DIFFUSION COEFFICIENTS—*Concluded*

Temperature = 91.0° F.

External vapour pressure = 27.2 mm. of Hg. = 75% relative humidity

Internal vapour pressure = 0.0 mm. of Hg.

Material	Thickness, cm.	Diffusance $\frac{D}{d}$ gm./24 hr./ sq. m./ mm. Hg.	Diffusivity $\frac{d}{d}$ gm./24 hr./ sq. m./ mm. Hg. cm.
Wood (Pine) B	1.29	2.17	2.80
Wood (Pine) B 1 coat white enamel paint		1.25	
Wood (Pine) B 2 coats white enamel paint		0.60	
Wood (Pine) B 3 coats white enamel paint		0.47	
Kraft paper (1 sheet)	0.010	51.8	
Kraft paper (2 sheets)		32.9	
Kraft paper (3 sheets)		24.7	
Kraft paper (4 sheets)		19.6	
Kraft paper (5 sheets)		16.5	
Kraft paper (5 sheets)		20.1	
Kraft paper (5 sheets)		19.0	
Kraft paper (7 sheets)		14.0	
Kraft paper (7 sheets)		11.8	
Kraft paper (8 sheets)		11.8	
Kraft paper (8 sheets)		10.2	
Black vulcanized rubber (Hardness 40)	0.201	0.060	0.012
Plasticized rubber hydrochloride	0.004	0.124	0.00049
30-30-30 paper A.	0.018	0.595	
30-30-30 paper B.	0.018	0.581	
Duplex Scutan 6-6 (Asphalt between two sheets of kraft paper)	0.018	0.307	
Scutan 0-14 (Kraft paper infused with asphalt on one surface) A.	0.018	2.79	
Scutan 0-14, B.	0.018	5.18	
Scutan 14—Kraft paper infused with asphalt on both surfaces, A	0.018	4.50	
Scutan 14, B.	0.018	5.11	
Black building paper, A black shiny paper completely infused with asphalt	0.044	0.122	
Asphalt felt, 15 lb., A felt building paper having soft dull appearance	0.081	4.38	
Pressed corkboard A	2.3	1.54	3.55
Pressed corkboard B	2.5	1.76	4.39
Plaster	3.4	8.81	30.2
Plaster board (Plaster between sheets of heavy paper)	0.94	22.8	
Rock wool (density 7 lb./cu. ft.)	9.0		152.0
Masonite Presdwood (Tempered)	0.33	3.17	
Masonite Presdwood	0.33	7.04	
Masonite Presdwood (5 thicknesses)		2.03	
Masonite Presdwood (7 thicknesses)		1.59	

No great accuracy is claimed for the results given in this table. Because of the practical application to which the results are to be put, no very great accuracy is required. The variation in the diffusion coefficient of different samples of the same material, and variations in the methods of construction in

buildings are so large that too great a refinement in the measurements is quite uncalled for. It is for this reason also that there need be no hesitation in using Fick's law for such measurements. Notwithstanding this, it was found that measurements on any one sample could be repeated accurately to two figures. But when different specimens were used the results were not so consistent. This was especially noticeable in the case of wood, which, as is quite evident, does not have a homogeneous structure. In all the specimens of wood tested, the moisture flow was transverse to the grain, but no precautions were taken to distinguish whether the flow was radial or tangential to the annual rings. The measurements recorded in this paper indicate that the flow of moisture through wood is a very complicated phenomenon. This bears out previous work (4, 7). It is quite definitely established that the moisture gradient in wood through which moisture is moving in a transverse direction departs quite substantially from a straight line, so that the use of Fick's law is quite unwarranted. This probably accounts for a great deal of the variations in the results obtained for wood under various conditions of measurement. In building construction, wood is always employed in the form of boards that are joined together with a tongue and groove, or an over-lap, or are simply butted together. In any case, cracks are bound to exist between the individual pieces, and it is exceedingly probable that by far the greater amount of moisture passes through these cracks; consequently, the amount passing through the wood itself is negligible. Thus, while the figures for wood are interesting for purposes of comparison, the diffusion coefficients in this case have little practical value. Before any reliable estimate can be made of the vapour transmission through a wooden wall, it will be necessary to obtain accurate data on the vapour transmission through cracks. These data are not yet available, so that one can only roughly estimate the vapour resistance of a wooden wall.

The resistance of wood, fibreboard and kraft paper have been measured at various thicknesses; the relation between the resistance and thickness for these three materials is shown in Figs. 5, 6, and 7, respectively. In these

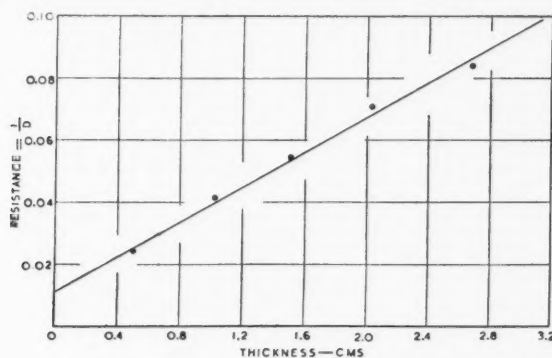


FIG. 5. *Fibreboard: Variation of resistance with thickness.*

figures the resistance of the material has been plotted against the thickness. The resistance is the reciprocal of the diffusance ($R = \frac{1}{D}$), and, according to Fick's law, should vary linearly with thickness. In all three figures it is seen that the points approach more or less closely to a straight line. Only in the case of wood does this line appear to pass through the origin. When the

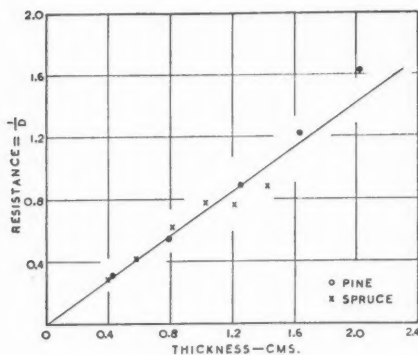


FIG. 6. Wood: Variation of resistance with thickness.

curve does not pass through the origin it indicates that there is a surface resistance to moisture transfer; in other words, even if the thickness of the material were zero there would remain some resistance. This means that an additional resistance exists in the air space in contact with the surface of the material, so that the vapour pressure drop across the sample is less than the total vapour drop between the desiccant and the external atmosphere [cf. (1) and (2)]. The effect, however, is insignificant for our purposes.

That the curve for wood appears to pass through the origin may be due to the relatively greater resistance of wood.

In Table II some results of previous measurements are reproduced for purposes of comparison. The results for rubber and plasticized rubber hydrochloride are included to show that the present results compare favour-

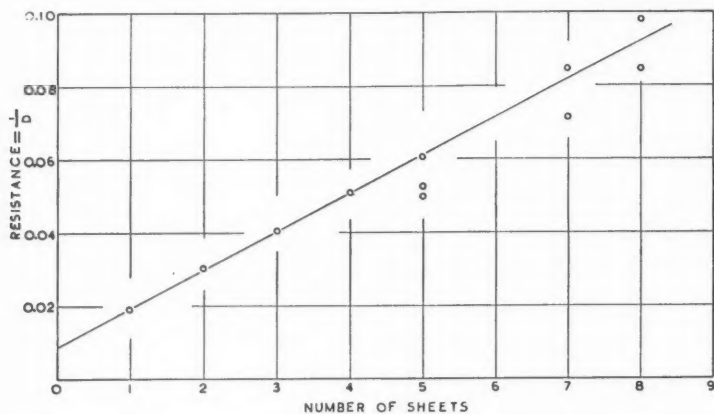


FIG. 7. Kraft paper: relation between number of sheets of paper and resistance.

ably with those of Taylor, Herrmann, and Kemp (8). Results from the very excellent paper on wood by Stillwell (7) have not been included since it is too difficult to extract a representative result. The reader is referred to the original paper, which gives an interesting theoretical discussion of moisture transfer through wood. Also, none of the data obtained by Wray and his co-workers (3, 10) on paint films are shown in Table II, as, to be of value, they would have to be reproduced in full. Here again reference should be made to the original papers. The results given by Miller (5) have been reproduced in full.

TABLE II
PREVIOUS MEASUREMENTS

Material	Thickness	Temp., ^o F.	V.P. difference, mm. of Hg.	<i>d</i>	<i>D</i>	Ref.
Rubber (soft vulcanized)	0.0354 cm.	77.0	Various	0.0158 to 0.0185		(8)
Plasticized rubber hydrochloride	0.0029 cm.	77.0	18.0 - 0.0	0.00036	0.126	(8)
Wood (Scots pine)	From 1 to 5 cm.	104.0	Av. up to 20 mm.	17.6		(4)
Wood (Western yellow pine)	0.635 cm.	80.6	25.4 - 0.0	1.48		(10)
Plaster base and plaster	0.75 in.				9.71	(5)
Fir sheathing	0.75 in.				1.94	(5)
Vapour barrier					0.53	(5)
Waterproof paper					32.4	(5)
Pine lap siding					3.24	(5)
Paint film					2.26	(5)
Celotex	0.75 in.				8.25	(5)
Brick masonry	4.0 in.				0.71	(5)

It has been necessary to change the units in nearly all cases. Miller, in his paper, has given very little indication of how his results were obtained. For some materials they differ widely from the present measurements. His figure for a vapour barrier is especially interesting. It is taken from a paper published by the Engineering Division of the Kimberley-Clark Corporation, entitled "The Practical Aspects of Condensation in the Building Industry." In this paper the statement is made that "Information now available leads to the recommendation that within the United States vapour seals are needed only in locations North of the Ohio River and that the seal or barrier used should transmit water vapour no faster than 0.40 gm./sq. m./hr. under a vapour pressure of 18 mm. of mercury." This is the figure quoted by Miller when the units are suitably changed. Unfortunately the Kimberley-Clark Corporation do not give the data on which this figure is based. In the following section of this paper, further considerations will be given to this question of a vapour barrier, and an endeavour made to estimate what value of vapour resistance is required before any material may be considered to constitute a vapour barrier.

Use of Diffusion Coefficients

In his paper (5), L. G. Miller has indicated how the diffusion coefficient of a material may be used to calculate the possibility of condensation in a wall. It is the intention now to extend this method and to apply the coefficients presented in this paper. It is especially desirable to indicate how the vapour barrier conception works in practice.

As indicated by Miller the possibility of moisture condensation is related to the temperature gradient through the wall. The fundamental equation for heat transfer, from which the temperature gradient can be determined, is:

$$H = \frac{kAt}{x} (T_1 - T_2)$$

where H is the quantity of heat transmitted in time t through a cross section of material of area A and thickness x when a temperature difference $T_1 - T_2$ is maintained across the material. The term k is the coefficient of conductivity. The method of applying this equation to a composite wall structure in order to obtain the over-all transmission is well known and is given in any standard book on heat transfer. The point to be emphasized is that Fourier's equation above is identical in form with Fick's law governing the vapour transfer, so that the same treatment may be applied to Fick's law to find the vapour gradient through the wall as is used with Fourier's law to obtain the temperature gradient. When these two gradients are known, the possibility of condensation can be immediately estimated. The dew-point at various positions in the wall can be plotted, and if at some point in the wall the existing temperature is below the dew-point corresponding to the humidity at this point, condensation will occur.

In order to carry through a calculation of the temperature and humidity gradients through a wall it is necessary to assume some typical conditions of temperature and humidity existing on the two sides of the wall. For the inside conditions a temperature of 70° F. with a relative humidity of 40% would seem to be a suitable choice. (This corresponds to a vapour pressure of 7.5 mm. of mercury). The temperature of 70° is an average indoor winter temperature, and one would seldom find a relative humidity greater than 40% when there is zero weather outside. The choice of suitable external conditions is not nearly so easy. In Canada, temperatures of -20° F. are quite common and in many cities temperatures much lower than this have been recorded. Except in extreme cases, however, these conditions do not last for a sufficient length of time to establish equilibrium conditions in a building, so that for our purpose it is not necessary to assume a temperature as low as -20°. However, to make the conditions more severe than would commonly be met in practice, we shall assume an external temperature of -10° F. and shall take the external vapour pressure as being 75% relative humidity at this temperature. (Vapour pressure = 0.42 mm. of mercury.)

For our purpose a typical wood frame wall will be considered. This consists of siding, building paper, sheathing, a 4 in. air space filled with rock

wool, and a finishing of plaster base and plaster on the inside. This type of wall, containing 4 in. of rock wool, furnishes just the conditions that are most conducive to moisture condensation, since, as has been pointed out by many authors, the high degree of insulation afforded by the rock wool maintains

TABLE III

—	C , B.T.U. /hr./sq. ft./°F.	$R = \frac{1}{C}$	Temp. drop, °F.	Actual temp., °F.	Saturated vapour pressure, mm. Hg.
External surface coefficient	6.00	0.17	0.8	-9.2	0.6
Siding, building paper, sheathing	0.50	2.00	9.2	0.0	1.0
Air space + rock wool	0.07	14.28	65.1	65.1	15.8
Wood lath + plaster	2.50	0.40	1.8	66.9	16.9
Internal surface coefficient	1.65	0.61	2.7	69.6	18.8

$$\text{Over-all resistance} = 17.46$$

$$\text{Over-all transmission} = \frac{1}{17.46} = 0.057 \text{ B.T.U./hr./sq. ft./°F.}$$

$$\text{Total temperature drop across the wall} = 70^\circ + 10^\circ = 80^\circ$$

$$\text{Total heat transmitted through 1 sq. ft.} = 0.057 \times 80 = 4.56 \text{ B.T.U./hr.}$$

the inside surface of the sheathing at a lower temperature than it would have if the insulation were less. Table III gives the data necessary to calculate the temperature gradient through such a wall, and indicates the method of computation.

The first column gives the conductance, C , of the material. The third column gives the temperature drop across the different sections of the wall; this is obtained by multiplying the total heat transmitted (4.56 B.T.U.) by the value of R in Column 2. The fourth column gives the actual temperature of the inside surface of these different sections. In the last column the saturated vapour pressures corresponding to the temperatures in the preceding column are given. The temperature gradient through the wall has been drawn in Fig. 8, and the saturated vapour pressure is also indicated. The saturated vapour pressure is not linear but is concave upwards.

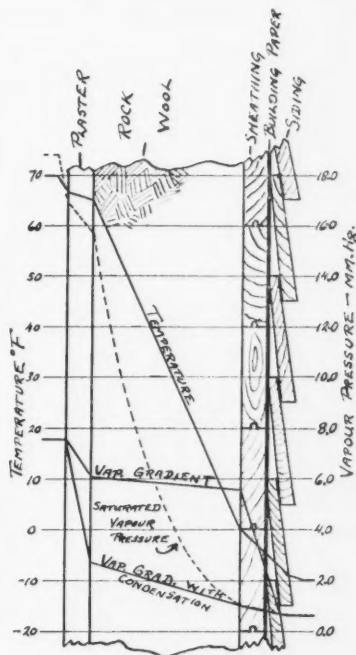


FIG. 8. Temperature and vapour gradient through a wall with no vapour barrier.

The next step is to calculate the vapour pressure drop through the wall, but here the difficulty of assessing the resistance of the wood sheathing and siding to moisture movement is encountered. As has been indicated previously, it is impossible, on the basis of the data at present available, to estimate, with any degree of accuracy, the vapour flow through the joints and cracks in the wood. In any case the individual joints will vary so greatly that anything but a very rough guess would be impossible. One thing is certain, and that is that the vapour resistance will be much less than that indicated by the flow through the wood itself. A study of Table I shows that a representative value of D for an inch of wood would be 0.50, but this figure is plainly much too low for a built-up wall. After considerable thought the conclusion was reached that if the resistance of the outer portion of the wall, *i.e.*, the sheathing, building paper, and paint, were taken equal to the measured value of the building paper alone, too great an error would not be introduced. In this way some allowance is made for the joints in the paper and the assumption is implicitly made that the resistance of the paint is not great, owing to weathering and cracking. The coefficients for the other portions of the wall may be used as measured since there the medium has no joints but is continuous. Table IV indicates the calculations involved in determining the vapour pressure drop through the wall.

TABLE IV

	D	$R = \frac{1}{D}$	Vapour drop, mm. Hg.	Actual pressure, mm. Hg.
Siding, building paper, sheathing	4.4	0.23	5.2	5.6
Air space + rock wool*	42.8	0.02	0.5	6.1
Plaster + plaster base ($\frac{3}{4}$ -in.)	15.9	0.06	1.4	7.5

 0.31

$$\text{Over-all moisture transmittance} = \frac{1}{0.31} = 3.2 \text{ gm./24 hr./sq.m./mm.Hg.}$$

$$\text{Total vapour pressure drop across wall} = 7.5 - 0.4 = 7.1 \text{ mm. Hg.}$$

$$\text{Total moisture transmitted per sq. m.} = 3.2 \times 7.1 = 22.6 \text{ gm./24 hr.}$$

* The factor used for rock wool is about $2\frac{1}{2}$ times that given in Table I to allow for the fact that the bats are not continuous.

The vapour gradient as given by the figures in the last column has been plotted in Fig. 8, where the saturated vapour pressure through the wall is also shown. Now, it is impossible for the actual vapour pressure at any point in a wall to exceed the saturated vapour pressure corresponding to the temperature at that point, because in that case condensation will occur until the vapour pressure has decreased to the saturated value. It is seen in the figure that the calculated vapour gradient is above the saturated vapour pressure in the outer portions of the rock wool, and it will be observed that for the inner surface of the sheathing the curve representing the vapour gradient

is 4.6 mm. of mercury above the saturated vapour pressure corresponding to the temperature of the sheathing. Under these conditions condensation will certainly occur. Since the vapour pressure gradient through the wall was calculated on the assumption that there was no condensation but a steady flow of moisture from the interior to the exterior, it must now be modified to allow for condensation. The vapour pressure in the wall can never be higher than the saturated vapour pressure. It is clear from the figure that the vapour pressure at the inner surface of the sheathing can never be greater than 1.0 mm. of mercury, which is the saturated vapour pressure corresponding to the temperature at this point. In the calculation of the vapour gradient given above, it was implicitly assumed that continuity of flow held, that is to say, that the amount of moisture leaving the wall at the exterior surface was exactly equal to, and neither greater nor less than, the amount of moisture entering the interior surface. When condensation takes place, this assumption is obviously untrue, and the vapour pressure gradient must adjust itself to allow for the condensation. It is necessary, therefore, to recalculate the vapour gradient on the assumption that moisture can move from the inside of a building to a point of condensation independently of any conditions existing beyond this point. Table V indicates the calculation of the vapour gradient from the interior to the surface of the sheathing under these conditions.

TABLE V

	D	$R = \frac{1}{D}$	Vapour drop	Vapour pressure
Air space + rock wool	42.8	0.023	1.7	2.7
Plaster + plaster base	15.9	0.063	4.8	7.5
		0.086	6.5	

$$\text{Over-all moisture transmittance} = \frac{1}{0.086} = 11.63 \text{ gm./24 hr./sq.m./mm. Hg.}$$

$$\text{Vapour pressure drop} = 7.5 - 1.0 = 6.5 \text{ mm. Hg.}$$

$$\text{Total moisture transmitted per sq. m.} = 11.63 \times 6.5 = 75.6 \text{ gm./24 hr.}$$

Under these conditions 75.6 gm. of moisture per sq. m. would move each day from the interior of the house to the point of condensation at the inside of the sheathing. However, the water (in this case it would be in the form of ice) would not accumulate quite so quickly as this, since there would be a tendency for some of it to continue to migrate towards the outside. The following calculation shows the amount of moisture transmitted.

	D	$R = \frac{1}{D}$
Siding, building paper, sheathing	4.38	0.228

$$\text{Vapour drop} = 1.0 - 0.4 = 0.6 \text{ mm. Hg.}$$

$$\text{Total moisture transmitted} = 4.38 \times 0.6 = 2.6 \text{ gm./24 hr./sq. m.}$$

Hence under the conditions outlined above, moisture would accumulate at a rate of approximately $75.6 - 2.6 = 73$ gm. per day per sq. m.

It is interesting at this point to note that, owing to the curvature of the saturated vapour pressure curve, it is possible for condensation to occur at points in the rock wool other than at the surface of the sheathing. For if the vapour pressure gradient in the rock wool has a greater slope than that of the saturated vapour pressure curve at the sheathing, then the curve of vapour pressure gradient must meet the saturated vapour pressure curve before the sheathing is reached. The movement of vapour then adjusts itself so that the gradient is tangent to the saturated curve at some point and follows the saturated curve from there to the surface of the sheathing. Since beyond the point of tangency the slope of the gradient steadily decreases (corresponding to the saturated vapour) there would be a tendency for moisture to accumulate at this point.

Now, it is obvious from the above that to prevent the accumulation of moisture it will be necessary to reduce the flow through the inner portion of the wall until it is equal to or less than that through the outer portions; that is to say, the resistance must be increased by the addition of a vapour barrier. The accumulation of moisture could be prevented just as well by decreasing the resistance of the outer portion of the wall. This could be done by providing vents through which the moisture could easily diffuse. Many people have advocated the use of a combination of the two methods, but since we are primarily interested in the mechanism of vapour barriers we shall confine ourselves to this aspect of the problem. We, therefore, assume that conditions remain the same on the outside of the rock wool, so that our problem is to reduce the flow of moisture through the inside of the wall to 2.6 gm. per 24 hr. per sq. m. Hence the vapour barrier must reduce the flow from 75.6 gm. to 2.6 gm., *i.e.*, by a factor of $\frac{75.6}{2.6} = 29$. Therefore the vapour barrier must

TABLE VI

—	D	$R = \frac{1}{D}$	Vapour drop	Vapour pressure
Siding, building paper, sheathing	4.4	0.23	0.58	1.0
Air space + rock wool	42.8	0.02	0.06	1.1
Vapour barrier	0.4	2.50	6.32	7.4
Plaster + plaster base	15.9	0.06	0.16	7.5
		2.81	7.12	

$$\text{Over-all moisture transmittance} = \frac{1}{2.81} = 0.36 \text{ gm./24 hr./sq. m./mm. Hg.}$$

$$\text{Total vapour drop across wall} = 7.5 - 0.4 = 7.1 \text{ mm. Hg.}$$

$$\text{Total moisture transmitted per sq. m.} = 0.36 \times 7.1 = 2.5 \text{ gm./24 hr.}$$

increase the resistance of the wall by a factor of 29. Since the present resistance of the interior of the wall is 0.086, the wall required must have a resistance of $0.086 \times 29 = 2.5$. This is approximately the resistance that is required in the vapour barrier. It represents a diffusance of 0.4 gm. per 24 hr. per sq. m. per mm. of mercury. The corresponding value given by the Kimberley-Clark Corporation was 0.53. When the assumptions in the calculations and the inaccuracies in the data are taken into account, these two values may be taken as being roughly equivalent. Any material having a diffusance in the neighbourhood of these figures may be considered as a vapour barrier when used under conditions such as those specified above.

It now remains to calculate the vapour gradient through the wall constructed with such a vapour barrier ($D = 0.4$). Table VI gives this calculation.

The vapour gradient through the wall, given in the last column, has been plotted in Fig. 9 along with the temperature and saturated vapour pressure. It is evident from this that there is now no possibility of moisture condensation.

The calculations above have been given to show how the diffusion coefficients can be applied to any wall to determine the possibility of moisture condensation. The figure obtained for a vapour barrier applies only to the one type of wall and only to the conditions outlined. It is hoped, however, that this presentation has in some degree clarified some of the points that have so long obscured the problem of moisture condensation.

Acknowledgment

The author wishes to express his indebtedness to C. St. Jacques and W. G. Martin, laboratory assistants at the National Research Council. The former has constructed the apparatus involved in these measurements, and the latter has done much of the routine weighing.

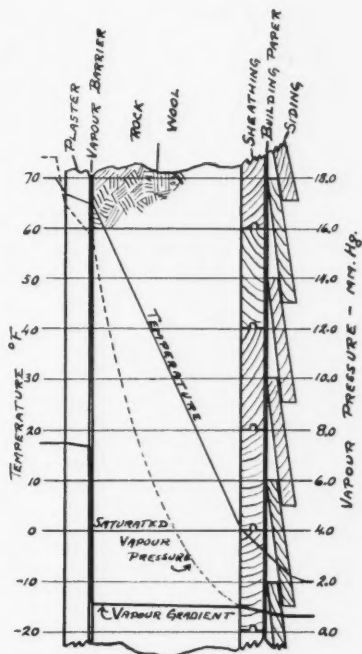


FIG. 9. Showing vapour gradient through a wall in which vapour barrier is placed.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XIX. *CORYDALIS OPHIOCARPA* HOOK. f. ET THOMS¹.

BY RICHARD H. F. MANSKE²

Abstract

Nine alkaloids have been isolated from *Corydalis ophiocarpa* only one of which, *ophiocarpine*, $C_{20}H_{21}O_5N$ (F39), is definitely characterized as new. It is a hydroxy-canadine in which the hydroxy group probably occurs in position 13. A second alkaloid, which may be new, is referred to as alkaloid F40. Berberine, its tetrahydro-derivative, namely *l*-canadine, and *l*-corypalmine constitute the remaining protoberberine alkaloids that were found. The presence of *l*-adlumine was established. This is the third plant from which it has been isolated. In addition, protopine, α -allocryptopine and cryptocavine, all of which contain the ten-membered ring characteristic of the first, were isolated.

In his latest treatment of *Corydalis*, Fedde (1) has arranged this genus into nine sections, many of which are divided into subsections. It is not the intention of the present author to call into question nor to deprecate such a classification. The fact that it serves as a useful instrument in identification is in itself sufficient justification for its adoption. There are, however, many moot points, and it is unlikely that any system thus far proposed is ultimate.

The possibility that the chemical constituents of plants may aid in their classification has been constantly kept in mind by the author. It is, nevertheless, impracticable to embark upon a program that would include the chemical examination of some 300 species of *Corydalis*. Aside from the labour involved there is the difficulty of securing material. It is feasible, however, to examine representatives of the sections and subsections, and the results obtained may be expected to indicate whether the classification is a natural one.

Thus far the author has investigated some sixteen species of *Corydalis* representing three sections and two subsections. It is expected that papers dealing with a number of these species will be published shortly.

Corydalis ophiocarpa Hook. f. et Thoms. (*C. streptocarpa* Maxim.) is dealt with in this communication. It is placed in the section *Eucorydalis* Prantl., subsection *Strictae* Fedde, and is native to Sikkim and to China from Yunnan and Szechwan to Kansu, Shensi, and Hupeh provinces. No American *Corydalis* spp. are placed in the same subsection although most of our species

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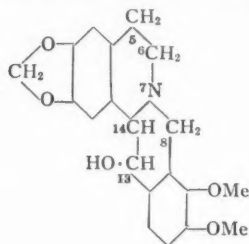
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Published as N.R.C. No. 787.

² Chemist, National Research Laboratories, Ottawa.

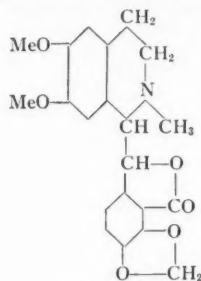
are included in the *Eucorydalis* section. In this connection it is pertinent to note that *C. aurea* (4) and *C. sempervirens* (3) are placed in the subsection *Eucapnoides* Fedde of section *Eucorydalis*. On the basis of their chemical constituents such a close relation is by no means certain. Of a total of some sixteen alkaloids in both species, only two, namely protopine and bicuculline, are present in each of the plants. The protoberberine alkaloids are entirely lacking in *C. sempervirens*. Owing to their widespread occurrence, their complete absence from a particular plant is regarded as significant.

C. ophiocarpa has thus far yielded nine alkaloids, and it resembles *C. aurea* mainly in containing the protoberberine alkaloids. If a reclassification on a chemical basis is attempted at this stage, *C. ophiocarpa* would occupy a position intermediate between *C. aurea* and *C. sempervirens*.

Of the nine alkaloids isolated, only one is definitely new. This is now termed *ophiocarpine* (F39). Analytical figures are in fair agreement with the empirical formula $C_{20}H_{21}O_5N$ containing two methoxyl groups. Two of the oxygen atoms are present in a methylene-dioxy group. A clue to the structure of the alkaloid and to the nature of the fifth oxygen atom was obtained when it was observed that boiling with strong hydrochloric acid resulted in dehydration with the formation of a yellow base which, on oxidation with iodine and subsequent reduction, yielded *dl*-canadine. Ophiocarpine therefore is a hydroxy-canadine in which the hydroxyl group is in one of the three possible positions, namely 8, 13, or 14. Positions 5 and 6 are not considered, because alkaloids in which these positions carry a substituent or are affected by iodine oxidations are unknown. That the hydroxyl is in position 8 is rendered improbable by the facts: (i) that ophiocarpine yields a colourless hydrochloride, and (ii) prolonged heating with alkali induces no



(I.)



(II.)

appreciable changes. A substance such as 8-hydroxy-canadine bears a close relation to hydrastinine, of which the hydrochloride is yellow and fluorescent and in which a Cannizzaro reaction is easily effected. A hydroxyl group in position 14 seemed *a priori* highly probable. In fact 14-hydroxy-canadine would be tautomeric with *N*-desmethyl-allocryptopine, a possible alkaloid not yet reported. It is clear, therefore, that the methiodide of 14-hydroxy-canadine would isomerize (tautomerize!) readily to allocryptopine hydroiodide.

When put to the experimental test, however, ophiocarpine methiodide could not be converted into allocryptopine. There remains therefore position 13 as the most probable for the hydroxyl group in ophiocarpine (I). Such a structure is not entirely without precedent. All the phthalide-isoquinoline alkaloids carry a potential hydroxyl in the benzyl moiety, its position there being strictly analogous to position 13 in the protoberberine alkaloids. Attention has been frequently drawn to the close relation between canadine and hydrastine. It is pertinent to note here that *l*-adlumine (5) has now been isolated from *C. ophiocarpa*. It has the structure (II) in which the positions of the methylene-dioxy and methoxyl groups are reversed with respect to ophiocarpine. Furthermore, *l*-canadine and its oxidation product, berberine, are present, as well as a trace of *l*-corypalmine. It is almost needless to mention that protopine was isolated, but it was accompanied by α -allocryptopine and a very small amount of cryptocavine. This is the fourth plant from which the last has now been isolated (5).

An alkaloid, referred to as F40, was obtained in small amounts. Its adequate identification or characterization is reserved for a later opportunity, as it has been found in larger relative amounts in another species now under investigation.

Experimental

The material for the present investigation was obtained from plants grown in a local garden and at the Central Experimental Farm, Ottawa, and the author takes this opportunity to express his indebtedness to Mr. John Adams of the Division of Botany for providing some facilities for growing the plants. *C. ophiocarpa* is an obligate biennial, and the experiments herein described were carried out with a composite collection comprising the first and second years' growths. There was available a total of 13.7 kilos of dried material. The procedure to which the author has repeatedly referred (2) was employed without modification for the isolation of the alkaloids, and the designations in the following summary have the significance previously adopted.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—ophiocarpine (F40), *l*-canadine, alkaloid F39.

BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-corypalmine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine, α -allocryptopine, cryptocavine, *l*-adlumine.

BSE and EES—Phenolic bases precipitated by carbon dioxide,—(not crystallized).

Ophiocarpine and Canadine

The washed and dried fraction (BC) consisted almost entirely of ophiocarpine, and its recrystallization from a large volume of methanol, in spite of its sparing solubility in this solvent, was found to be the best method of purification. A prior washing with cold methanol served to remove a small amount of *l*-canadine, which was obtained pure as the hydrochloride, regene-

rated from the latter, and recrystallized from methanol (0.01%). Almost colourless fine crystals melting at 135° C.* were obtained. $[\alpha]_D^{22} = -308$ ($c = 0.28$ in methanol). Calcd. for $C_{20}H_{21}O_4N$: C, 70.80; H, 6.20; N, 4.13; OMe, 18.20%. Found: C, 70.80, 70.68; H, 6.41, 6.28; N, 4.45, 4.37; OMe, 18.39, 18.01%.

A specimen was oxidized in ethanol with iodine, and the resulting quaternary iodide reduced with zinc in acetic acid. The *dl*-canadine thus obtained melted at 171° C., either alone or in admixture with a specimen prepared from berberine.

The once recrystallized ophiocarpine (yield, 0.25%) was recrystallized again from methanol, and was thus obtained in large stout prisms melting sharply at 188° C. The hydrochloride is colourless and sparingly soluble in cold water, and the base regenerated from it, and recrystallized as before, melted at the same temperature. It was also recrystallized by evaporating its solution in chloroform to a small volume and adding methanol. The melting point was not changed. $[\alpha]_D^{24} = -284^\circ$ ($c = 0.4$ in chloroform). Found: C, 68.00, 67.91; H, 6.04, 6.02; N, 4.30, 4.22; OMe, 15.99, 15.81%. Calcd. for $C_{20}H_{21}O_5N$: C, 67.60; H, 5.92; N, 3.94; OMe, 17.46%. The *methiodide* was slowly formed in a chloroform-methanol solution containing methyl iodide. After recrystallization from boiling water it melted to a black mass at 271° C. It also crystallized from the hot aqueous solution in the presence of ammonia or of potassium hydroxide.

Protopine and α -Allocryptopine

The fraction (BS) was dissolved in chloroform and the filtered solution (charcoal) evaporated to a small volume. The addition of hot methanol and a nucleus induced rapid crystallization of protopine, which was obtained pure by recrystallization (yield 0.19%).

The methanolic mother liquor was boiled with charcoal and evaporated to a small volume. A second crop of protopine crystallized and was filtered off. The addition of a crystal of α -allocryptopine to the filtrate induced the crystallization of this base. It was slightly contaminated with protopine, from which it was separated by recrystallization from much hot methanol. It melted at 160° C., either alone or in admixture with an authentic specimen of α -allocryptopine (yield 0.01%).

l-Adlumine and Cryptocavine

The mother liquor from the separation of the protopine and α -allocryptopine was evaporated and the residue dissolved in dilute hydrochloric acid. The turbid solution was filtered through charcoal, basified with ammonia, and extracted with much ether. The residue from the combined extract was dissolved in a small volume of methanol, from which a copious crop of crystals separated in the course of several days. This was a mixture and consisted of protopine, α -allocryptopine, and *l*-adlumine. The last was separated as follows. A chloroform solution of the mixture was evaporated to a thin

* All melting points are corrected.

resin, which was then dissolved in boiling methanol. A nucleus of pure *l*-adlumine was added. Crystallization of the large elongated hexagons was immediate, and the crystals were filtered off before the other bases crystallized. A second recrystallization from chloroform-methanol yielded *l*-adlumine melting sharply at 180° C., either alone or in admixture with authentic specimens from *C. sempervirens* or *C. scouleri*. The total yield was 0.03%.

The mother liquor from the crystallization of *l*-adlumine on long standing deposited a base contaminated with several groups of protopine crystals. The latter were separated by means of a spatula and the main base was recrystallized from chloroform-methanol. A repetition of the process yielded fine colourless needles melting at 223° C. (yield, 0.005%). Admixture with a specimen of cryptocavine from other sources did not lower the melting point, and the optical rotation in chloroform was zero. The colour reaction in sulphuric acid was that of the protopine group.

l-Corypalmine

The fractions (EC, BCE, and EEC) yielded a small amount of a crystalline base when left in contact with methanol. The base was recrystallized from chloroform-methanol and obtained in colourless stout prisms which, either alone or in admixture with a specimen of *l*-corypalmine from *Dicentra oregana*, melted at 230° C., some darkening taking place several degrees lower. The same alkaloid has been obtained in larger amounts from other species under investigation, and its positive identification as *l*-corypalmine will be described in detail in an early communication. The yield in the present case was considerably less than 0.01%.

Berberine

When the residue from the chloroform extract (C) of the aqueous acid solution was extracted with hot water and the filtered solution allowed to cool, a copious yield of a sparingly soluble hydrochloride was obtained. It was recrystallized again from hot water (yield, 0.05%), and a portion of it reduced with zinc dust in acetic acid. The regenerated base was recrystallized from methanol and identified as *dl*-canadine by melting point and mixed melting point (170° C.).

That berberine is contained as such in the living plant is highly probable because of the yellow colour of the sap. In autumn the leaves also take on an orange hue. It seems therefore improbable that oxidation of the *l*-canadine during the process of drying and extracting is the sole source of the berberine.

Alkaloid F40

The mother liquor from the recrystallization of the berberine hydrochloride was concentrated somewhat. On cooling, a mixture separated. This was redissolved in warm water, and an excess of ammonia was added. After cooling, the mixture was filtered and the precipitate washed with warm water until the filtrate was colourless, a procedure that served to remove the berberine. The dried precipitate was recrystallized twice from chloroform-

methanol; it then melted at 196° C. This base, *alkaloid F40*, has also been obtained from *C. cheilanthifolia*; its further examination will be detailed in connection with this plant.

Fumaric acid was isolated in small amounts from the ether extract (LC).

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XX. *CORYDALIS MICRANTHA* (ENGELM.) GRAY AND *CORYDALIS CRYSTALLINA* ENGELM.¹

BY RICHARD H. F. MANSKE²

Abstract

Chemical examination of *C. micrantha* and of *C. crystallina* has shown that their relation is not as close to *C. aurea* as taxonomic classification would suggest. *C. micrantha* was found to contain protopine, *l*-tetrahydro-palmatine, capaurine, capauridine, scoulerine, and three unidentified phenolic alkaloids (F41, F42, and F43). *C. crystallina* yielded only a small amount of total bases from which protopine, bicuculline, and capnoidine were isolated.

The two plants named in the title are evidently closely related taxonomically. Various authors have regarded them as varieties of *Corydalis aurea* Willd.; hence *C. micrantha* (Engelm.) Gray has been referred to as *C. aurea* var. *micrantha* Engelm. or *C. aurea* var. *australis* Chapm., and *C. crystallina* Engelm. is synonymous with *C. aurea* var. *crystallina* Torr. et Gray.

In view of the results of the chemical investigation that forms the subject of this paper, such an extremely close relation is not indicated. *C. micrantha* has yielded eight alkaloids, only four of which, namely protopine, *l*-tetrahydro-palmatine, capaurine and capauridine, are also present in *C. aurea* (3). The remaining four alkaloids include scoulerine and three alkaloids, F41, F42, and F43, whose further characterization or identification is dependent upon more material or upon their isolation from other sources.

The small quantity of *C. crystallina* permitted only a preliminary investigation. In addition to protopine there were isolated bicuculline and capnoidine. The last was not found in *C. micrantha* nor in *C. aurea*, and *C. crystallina* has now been found to be the best source of this rare but fairly widely distributed alkaloid. The tetrahydro-protoberberine alkaloids appear to be almost completely absent. It would therefore appear that *C. crystallina* is more closely related to *C. sempervirens* (2).

Experimental

The materials for the present investigation were collected in Texas and kindly placed at the author's disposal by Dr. Glen A. Greathouse, College Station, Texas, to whom grateful thanks are extended. After drying and grinding, the weights were,—*C. micrantha*, 1740 gm. and *C. crystallina*, 1780 gm. The following is a summary of the isolated alkaloids and the fractions from which they were obtained (1), the names in parentheses referring only to alkaloids found in *C. crystallina*.

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Base hydrochlorides extracted from aqueous solution by means of chloroform,—

BC—Non-phenolic bases,—*l*-tetrahydro-palmatine (bicuculline).

BCE and EEC—Phenolic bases precipitated by carbon dioxide,—capaurine, capauridine, alkaloid F42, alkaloid F43.

Base hydrochlorides not extracted from aqueous solution by means of chloroform,—

BS—Non-phenolic bases,—protopine (protopine, capnoidine).

BSE and EES—Phenolic bases precipitated by carbon dioxide,—scoulerine, alkaloid F41.

l-Tetrahydro-palmatine

This alkaloid was purified as the sparingly soluble hydrochloride from fraction (BC), and the liberated base was recrystallized from methanol. It was obtained in fine colourless crystals which melted at 142° C.,* and in admixture with a specimen of *l*-tetrahydro-palmatine from *C. aurea* there was no depression in melting point. $[\alpha]_D^{27} = -281^\circ$ ($c = 2$ in 95% ethanol). The yield was 0.3%.

It has now been observed that *l*-tetrahydro-palmatine, when recrystallized from ether, yields the hydrate which melts with effervescence at 115 to 116° C. This has been found to be identical with an alkaloid previously regarded as new and described as caseanine (5). Mixed melting point determinations of the respective hydrates as well as of the bases recrystallized from methanol showed that they were identical. The optical activity of "caseanine" was found to be identical with that of *l*-tetrahydro-palmatine, and therefore the name, caseanine, no longer has validity. The isolation of bicuculline from fraction (BC) (*C. crystallina*) followed the procedure repeatedly outlined. The yield of pure base was 0.02%. It melted at 177° C. A portion was converted to the higher melting form (196° C.), and both forms were compared with authentic specimens.

Capaurine, Capauridine, Alkaloid F43, and Alkaloid F42

Fraction (BCE) contained coloured impurities which were removed by means of charcoal in methanol solution, and then fraction (EEC) was added. In the course of several days a small amount of fine colourless needles separated. These were recrystallized twice from chloroform-methanol; they then melted at 208° C., either alone or in admixture with a specimen of capauridine from *C. aurea*. The yield of capauridine was 0.006%. The filtrate from the capauridine was evaporated somewhat, and in the course of several days another base (about 0.02 gm.) was deposited. It was recrystallized from chloroform-methanol and obtained in brilliant stout prisms which began to shrink at 226 to 228° C. and melted to a brown tar at 230° C. It does not appear to be identical with *l*-corypalmine, with alkaloid F25, or with alkaloid F32. Unfortunately the analyst lost the sample after having determined nitrogen and methoxyl, so that a carbon-hydrogen analysis could not be carried out

*All melting points are corrected.

with the material at hand. The results obtained, however, indicate $C_{20}H_{23}O_4N$. Found: N, 4.30, 4.39; OMe, 26.42, 25.96%. Calcd. for $C_{20}H_{23}O_4N$: N, 4.10; 3OMe, 27.27%.

Alkaloid F43 dissolved in sulphuric acid to yield a colourless solution which, on warming, became yellowish-pink. Progressive heating changed the colour of this solution to orange, then brown, and finally deep purple.

The solvent was removed from the mother liquor from which alkaloid F43 had crystallized, and the residue dissolved in dilute hydrochloric acid. The filtered solution (charcoal) was basified with ammonia, and the liberated bases were extracted with ether. The residue from the ether crystallized readily. It was extracted with several successive portions of hot methanol and the residue recrystallized from chloroform-methanol. Alkaloid F42 as thus obtained consists of fine colourless needles melting at 239° C. with a little previous darkening. Its colourless solution in sulphuric acid only became orange on heating but changed to purple on cooling.

The combined methanolic extract from the purification of alkaloid F42 was evaporated to a small volume. On cooling, pale yellow stout prisms melting at 162 to 163° C. were obtained. When recrystallized again from hot methanol, the base melted at 164° C. Its appearance suggested its identity with capaurine, and a mixed melting point determination (164° C.) proved it.

Protopine and Capnoidine

Except for possible traces of other alkaloids, the fraction (BS) from *C. micrantha* consisted of protopine, which was obtained pure by recrystallization and authenticated by comparison with a genuine specimen. (Yield, 0.06%).

The fraction (BS) from *C. crystallina* was converted into the hydrochloride and most of the protopine isolated as this salt. The regenerated base was properly authenticated, and, together with that obtained from the mother liquor, there was a yield of 0.21%. The filtrate from the protopine hydrochloride was basified with potassium hydroxide and the liberated bases were washed and dried. The mixture was dissolved in chloroform and the filtered solution evaporated to a resin. In contact with methanol the resin crystallized at once. The filtered mixture was redissolved in chloroform, evaporated to a small volume, and treated with hot methanol. The addition of a crystal of protopine induced immediate crystallization of this alkaloid, and when no more appeared to be separating the mixture was filtered. The filtrate deposited almost immediately a second base melting at 235° C. When this was recrystallized from chloroform-methanol, colourless stout prisms melting at 235 to 237° C. were obtained. In admixture with a similarly purified specimen of capnoidine from *C. sempervirens* (m.p. 236 to 238° C.) there was no observable depression in melting point. The yield was 0.025%.

Scoulerine and Alkaloid F41

The fraction (BSE) in methanol was heated with a liberal quantity of charcoal, the filtrate added to fraction (EES), and sufficient methanolic hydrogen

bromide added to render the solution acidic. In the course of several days a sparingly soluble salt separated. The free base was regenerated from an aqueous solution of the salt and extracted with ether. The residue from the extract crystallized in contact with methanol-ether. It was washed with a little ether; it then melted at 195 to 196° C. In admixture with a specimen of scoulerine from *C. scouleri* (4) it melted at 198 to 200° C. when placed in a bath preheated to 180° C. (Yield, about 0.01 gm.).

The filtrate from the scoulerine hydrobromide was heated to expel organic solvents, the residue dissolved in hot water, and the turbid solution filtered. A sparingly soluble hydrobromide crystallized from the filtrate in 24 hr. The base was regenerated by means of ammonia and extracted with ether. The residue from the ether crystallized in contact with methanol-ether. It was recrystallized by adding ether to a concentrated methanol solution. Colourless aggregates of fine prisms of alkaloid F41, melting at 177° C. to a red liquid, were thus obtained. It dissolves in cold sulphuric acid to form a colourless solution which, on gentle warming, turns pink. Further heating yields only a brown solution which, however, becomes deep violet on cooling. The yield was about 0.05 gm.

Fumaric acid was isolated from both plants (fraction LC).

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THE ROLE OF COPPER IN THE DETERIORATION OF RUBBER¹

BY R. R. McLAUGHLIN² AND G. P. BEAL³

Abstract

Dried rubber latex containing graded amounts of copper ammonium acetate was aged in air (I) and in nitrogen (II), and the deterioration followed by determining the acetone-soluble resin, r , and the relative viscosity of benzene solutions, v . For (I), r decreased slightly for a time, varying inversely with the amount of copper present, increased rapidly to a maximum, and finally decreased somewhat. The value of v decreased rapidly at a rate varying directly with the copper content. For (II), r remained constant, while a slight decrease in v , attributed to traces of oxygen, was of a different order from v for (I). It was concluded that copper, per se, is not deleterious but acts by catalytic oxidation.

As stated in a review of the question by Dufraisse (3, p. 466), oxygen is responsible for at least the more obvious, harmful changes in rubber, as a number of investigators have found slight or negligible deterioration in the absence of oxygen. The deleterious effect of copper on rubber is well known, having first been noted by Miller (4), and it has generally been supposed that this is due to oxidation catalyzed by the copper, an assumption which is in harmony with the above conclusion. In order to test this assumption, this investigation was undertaken. It should be noted that a different conclusion has been reached by Buizov, Molodenskii and Mikhailov (2), who are of the opinion that copper, per se, causes a molecular and micellar dis-aggregation resulting in stickiness, and that oxygen is not necessary for this process.

The method employed to determine whether the deleterious action of copper is to be ascribed to depolymerization alone or to catalytic oxidation was to carry out parallel experiments involving the addition of cupric ammonium acetate to rubber latex in the absence and in the presence of oxygen, for if it were due to the former cause, there should be evidence of depolymerization in the absence of oxygen. Depolymerizing action was followed by means of relative viscosity measurements of resulting benzene solutions, and oxidation by means of acetone extraction of the resulting resins.

Preparation of Samples

Experimental

Samples were prepared containing 0.10, 0.20, 0.25% copper, by adding cupric ammonium acetate solution (0.00653 gm. Cu per cc.; pH, 10.5) to approximately 75 gm. of 60% rubber latex (pH, 9.6). Samples (10 gm.) of the resulting mixture were placed in Petri dishes 9 cm. in diameter.

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The samples to be aged in nitrogen were dried at 35° C. in an atmosphere of nitrogen (freed from oxygen by passage over copper at 300° C.) for three days. The pressure was maintained at about 500 mm. for the first six hours to prevent frothing, and reduced to 50 mm. for the remaining period. The samples were then transferred to a nitrogen-filled, glass container.

The samples to be aged in air were first dried in air at 23° C. for 24 hr., then in the vacuum oven at 32° C. and 50 mm. for two and one-half days. The first samples for measurement were taken after they had been in the drying oven one and one-half days.

Both sets of samples, in Petri dishes, were placed in a room with northern exposure and with rather low light intensity. The samples in air were protected from dust by means of a filter paper suspended two inches above the surface of the dishes; this allowed free access of air.

Acetone Extraction

Acetone was purified by the method of Werner (5) to remove peroxides, and the extraction was carried out for 48 hr. in an Underwriters' extraction apparatus.

Relative Viscosity Measurement

Approximately 0.6 gm. samples were weighed out, placed in glass stoppered bottles, and benzene (distilled from sodium) was added in the ratio of 100 gm. of benzene to 1 gm. of rubber. The air was displaced by nitrogen, and the bottles were shaken for 5 to 15 days (as indicated in Table II) till solution was complete. Samples (10 cc.) of the resulting solution were placed in an

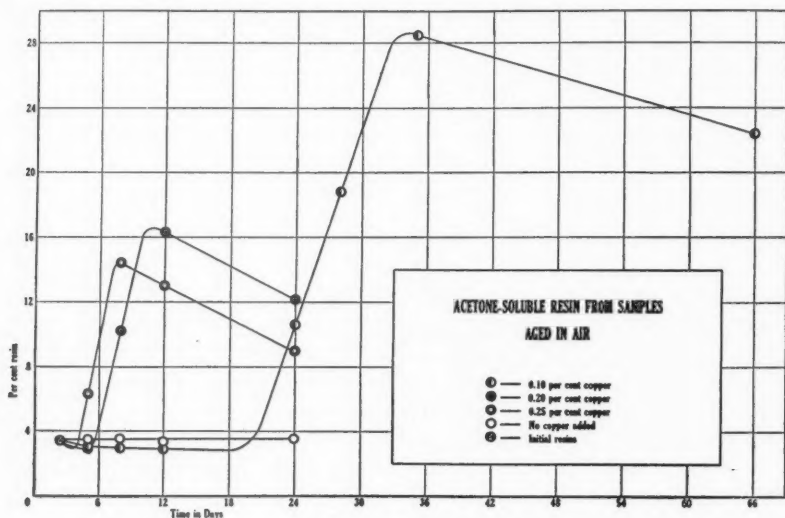


FIG. 1. Graphical presentation of results from Table I, for samples aged in air.

Ostwald viscosimeter immersed in a water thermostat at 25° C., and the relative viscosity was determined by noting the time of flow in seconds. In this time, 3.75 cc. of solution passed through 9 cm. of 1 mm. bore capillary, under a mean head of 10.2 cm.

Samples Aged in Air

The curves in Fig. 1 show that there are three distinct stages in acetone-soluble resin production in samples, containing copper, aged in air. (a) A period during which the amount of acetone-soluble resin present decreases. This decrease is slight, though it is believed to be significant, and it may be associated with the destruction by the copper of the natural inhibitors of oxidation mentioned by Whitby, Dolid, and Yorston (6) and Bruson, Sebrell, and Vogt (1). The duration of this period varies inversely with the amount of copper present in the samples. (b) A period during which resin production begins suddenly and rapidly. During this period the samples become very tacky on the surface, but the rubber next to the glass does not seem to have suffered, a result to be expected from the experiments in nitrogen. (c) A period during which the amount of acetone-soluble resin decreases owing to the surface tackiness giving place to a hard skin of material only partially soluble in acetone and benzene.

Correlation of the results given in Tables I and II shows that decrease in relative viscosity runs, in general, parallel with increase in the amount of acetone-soluble resin. The figures indicate that the effect of the copper precedes the actual liberation of acetone-soluble resin, as the relative viscosity begins to fall before the amount of acetone-soluble resin begins to rise. It is likely that this is

Discussion

TABLE I
ACETONE EXTRACT (RESIN)

Time, days	Copper in samples, %			
	0	0.10	0.20	0.25
Resin, %				
<i>Aged in air</i>				
2½	3.32 3.36	3.38 3.51	3.36	3.46 3.37
5	3.31 3.55	3.13 3.13	2.85 2.95	5.31 5.96
8	3.33 3.77	2.96 2.96	10.9 9.5	14.25 14.56
12	3.43 3.22	2.78 2.98	18.4 14.3	12.9 13.1
24	3.39 3.69	10.4 10.8	12.0 12.3	7.7 10.3
28		18.5 19.2		
35		28.0 28.9		
66		23.8 21.0		
<i>Aged in nitrogen</i>				
3	3.75 3.88	3.78 3.72	3.72 3.84	3.47 3.73
18	3.27	3.28	3.25	3.26

associated with what might be termed the induction period, (*a*), mentioned above. It should be noted, however, as will be shown presently, that this step does not appear to take place in the absence of oxygen.

Samples Aged in Nitrogen

As would be expected, the amount of acetone-soluble resin present in the samples aged in nitrogen remained constant throughout.

As the results in Table II show, there is a slight decrease in relative viscosity with time, but this decrease is of a totally different order from that of the samples aged in air. It might be concluded from the decrease, however, that the copper alone has some effect, especially as the relative viscosity

TABLE II
RELATIVE VISCOSITY MEASUREMENTS*

Time, days	Copper in samples, %			
	0	0.10	0.20	0.25
	Time of flow, in seconds			
<i>Aged in air</i>				
2½	72.0	42.8	13.8	12.0
7	73.4	29.6	5.6	5.2
12	70.2	13.2	6.0†	6.2†
26	66.4	4.2	7.4†	7.2†
<i>Aged in nitrogen</i>				
7	108	72.2	65.4	51.2
26	108	79.4	53.0	51.8
42	102	60.2	47.2	44.8
164		64.2	54.2	43.2

Time of flow for benzene, 3.7 sec.

*Times allowed for samples to dissolve in benzene:

Aged in air, without copper, 12 days; aged in air with copper, 4 days.

Aged in nitrogen without copper, 15 days; aged in nitrogen with copper, 10½ days.

†Insoluble resin present.

at the start varies inversely with the amount of copper present. Another explanation is indicated by the remarks of Dufraisse (3, pp. 463-466) concerning the difficulty of removing all traces of oxygen from rubber samples. It is certain that traces of oxygen either free or in combination, from which it is readily available, would remain in the present case, even though drying was carried out in an atmosphere of purified nitrogen. These traces of oxygen might be quite enough in the presence of copper to account for the diminished viscosity, and it would be expected that the effect would be more pronounced the higher the amount of copper present; and as the residual oxygen is greater since it is unlimited, in those samples dried in air, than in the ones dried in nitrogen, this is a probable explanation for the greater relative viscosity, at the start, of the copper-free samples aged in nitrogen compared with the copper-free samples aged in air. The reason for the relative viscosity of the samples containing copper and aged in nitrogen being progressively lower than that of the copper-free samples, as the amount of copper is increased, is undoubtedly related to this, as the curves in Fig. 1 show that the action of oxygen becomes evident sooner as the amount of copper is increased. In general it is believed that in experiments of this kind a good deal of the deterioration takes place within

As the results in Table II show, there is a slight decrease in relative viscosity with time, but this decrease is of a totally different order from that of the samples aged in air. It might be concluded from the decrease, however, that the copper alone has some effect, especially as the relative viscosity at the start varies inversely with the amount of copper present. Another explanation is indicated by the remarks of Dufraisse (3, pp. 463-466) concerning the difficulty of removing all traces of oxygen from rubber samples. It is certain that traces of oxygen either free or in combination, from which it is readily available, would remain in the present case, even though drying was carried out in an atmosphere of purified nitrogen. These traces of oxygen might be quite enough in the presence of copper to account for the diminished viscosity, and it would be expected that the effect would be more pronounced the higher the amount of copper present; and as the residual oxygen is greater since it is unlimited,

a short time after mixing because of the presence of oxygen during the initial evacuation and drying.

A qualitative observation in support of the conclusions reached is that the samples containing copper and aged in nitrogen had, even after 150 days, retained their initial elasticity and had not become tacky. Furthermore, the samples aged in nitrogen retained their original pale green colour, whereas the samples aged in air turned brown, like those of Buizov, Molodenskii, and Mikhailov (2).

It will be noticed that the times taken for the samples to go into solution provide a rough measure of the relative viscosity to be expected, and support the belief that, in the absence of oxygen, copper has no deleterious action.

Thus, the evidence presented indicates that the deleterious action of copper is not due to depolymerizing action merely because of its presence, but is due to oxidation catalyzed by the copper.

Acknowledgments

This research was proposed and the preliminary work carried out by W. R. Grant as his thesis for the degree of B.A.Sc., obtained in this Department in the academic year 1935-36. The preliminary work was continued by A. B. Lewis for his B.A.Sc. degree in 1936-37.

The completion of the work was made possible by a grant from the School of Engineering Research, University of Toronto.

The rubber latex used was supplied by the Dunlop Tire and Rubber Goods Company, Limited, Toronto.

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SOME OBSERVATIONS ON THE DETERMINATION OF IRON AND COPPER IN BIOLOGICAL MATERIAL BY PHOTOELECTRIC COLORIMETRY¹

BY W. E. PARKER² AND F. P. GRIFFIN³

Abstract

The dipyriddy method of estimating available iron has been modified so that it can be applied directly to coloured extracts of plant tissues. By combining the dipyriddy method for iron with the carbamate method for copper, interference of iron with the copper determination has been eliminated and the simultaneous estimation of iron and copper on the same sample made possible.

Introduction

In a study being made in this laboratory of the distribution of iron in plant tissue, it was observed that Elvehjem's (4, 10) method for available iron gave erratic results when applied to acid extracts of leaf tissues. Investigation showed that the discrepancies were due to the introduction of lead acetate as a clarifying agent. It was found that this difficulty could be readily overcome by the use of the Evelyn photoelectric colorimeter (6), and a suitable filter, since then there is no need to clarify the solutions whose colour intensities are to be measured.

The total copper content of the tissues was determined by the carbamate method. McFarlane (9) suggests that isoamyl alcohol be used as the solvent for the yellow copper carbamate complex. However, iron, if present, interferes by the formation of a yellow-brown carbamate salt, likewise soluble in isoamyl alcohol. This difficulty can be overcome by the preliminary conversion of the iron into an un-ionized ferric complex which does not react with the carbamate reagent (3, 7, 9).

Ferrous dipyriddy is un-ionized, and is completely insoluble in isoamyl alcohol. Conversion of the iron into this form should therefore be a suitable method of eliminating its interference with the carbamate reaction. As values for both total iron and copper were desired, it occurred to the authors that the use of dipyriddy, according to Hill's method (8), might permit the simultaneous determination of iron and copper in the one solution. Preliminary experiments showed that the addition of dipyriddy and a reducing agent to a solution containing both iron and copper, followed by the addition of carbamate and extraction with isoamyl alcohol, gave a clear pink aqueous layer and a clear golden-yellow alcohol layer. Measurements of the intensity of the two colours showed that both iron and copper could be recovered quantitatively, even when one was present in large excess.

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The two procedures are described below; that for the combined copper and iron determinations is given in some detail, as there is no reference in the literature to the application of the photoelectric colorimeter to the determination of copper by the carbamate procedure. The golden-yellow colour of the copper carbamate salt is very difficult to measure in an ordinary colorimeter, and it is found that the photoelectric type of instrument increases the accuracy and extends the range of the method.

Modified Procedure for Determining "Available Iron"

Duplicate samples of about 0.2 gm. of the dried and finely ground tissue were weighed into 6 by 1 in. Pyrex test tubes, 10 ml. of 10% acetic acid and 0.1 gram of sodium hydrosulphite* were added, and the tubes heated in a boiling water bath for 15 min. The acetic acid extracts were decanted through Jena glass filters into 50 ml. volumetric flasks and the residues extracted twice more for five-minute periods with the same quantity of acetic acid, and finally with 5 ml. of distilled water. Tests showed that further extraction did not increase the amount of soluble iron. The combined extracts were made up to volume with normal ammonium acetate solution of pH 6.4.

After tubes containing pipetted aliquots of these solutions had been placed in the photoelectric colorimeter fitted with an Evelyn 520 filter, the instrument was adjusted to give a maximum scale deflection of the galvanometer. Exactly 0.5 ml. of a 0.2% solution of α - α' -dipyridyl in 10% acetic acid was then added, the contents of the tube were well mixed, and the reading of the galvanometer again noted. Any decrease in the galvanometer reading was attributed to the presence of ferrous dipyridyl. The iron content of the aliquot was obtained from a calibration curve (5), allowance being made for the dilution by the 0.5 ml. of dipyridyl reagent. The slight error caused by the dilution of the leaf pigments by the reagent was found to be negligible.

Simultaneous Determination of Total Iron and Copper

The strongly acid solution obtained by the wet digestion of the sample (1) was diluted with distilled water and boiled for two minutes to ensure that all the iron was in a form that would react with dipyridyl (2). It was then filtered into a 50 ml. volumetric flask through an ash-free filter paper to remove any siliceous matter which might have been present. To the clear solution were added 0.5 ml. of *p*-hydroxyphenylglycine solution, 1 ml. of α - α' -dipyridyl reagent and then concentrated ammonium hydroxide until the red colour of the ferrous dipyridyl developed. Normal ammonium acetate solution was added to make the mixture almost up to volume, followed by two drops of a 1.5% aqueous solution of sodium diethyldithiocarbamate, and the whole was finally made up to volume with the acetate solution and well mixed. This order of adding the reagents was found to give the most satisfactory results.

* In later work 0.5 ml. of a 0.1% solution of *p*-hydroxy-phenylglycine in 0.4 *N* sulphuric acid was used as a reducing agent. Campbell and Dauphinee's (1) observations of its advantages have been fully confirmed.

To a 10 ml. aliquot of this solution in a dry Evelyn colorimeter tube were added exactly 5 ml. of pure isoamyl alcohol. The tube was stoppered with a paraffin-coated cork and the contents mixed by gentle shaking for one-half minute. A clear separation between the two layers took place on standing at room temperature for 15 to 30 min.; centrifuging at 1500 r.p.m. for 15 to 30 sec. gave the same result and avoided the possibility of errors arising from evaporation of the alcohol. It was found that there was no danger of breakage if the colorimeter tubes were fitted by means of cork stoppers into 100 ml. centrifuge tubes.

At this point the two layers can be separated completely and the coloured solutions compared with standards in an ordinary colorimeter. However, when an Evelyn photoelectric colorimeter is available it is much more accurate and convenient to make the measurements without carrying out the separation. In this way all possibility of mechanical loss is avoided, and the advantages of the photoelectric colorimeter for measuring the yellow colour are obtained.

To permit measurements of the two phases in one colorimeter tube, the Bakelite sleeve in which the tubes are inserted was replaced by one having

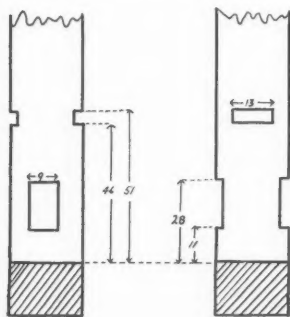


FIG. 1. Sketch of modified sleeve used in the Evelyn Photoelectric Colorimeter for simultaneous iron and copper determinations. All dimensions are given in millimetres.

two sets of apertures at right angles to each other and accurately located so that the lower aperture was opposite the aqueous phase and the upper aperture opposite the alcohol phase when the colorimeter tube was inserted in it. The dimensions of the tube, which was constructed of Bakelite tubing, are shown in Fig. 1.

The special sleeve was placed in the colorimeter so that the lower aperture was opposite the light source, an Evelyn 520 filter was inserted, and the concentration of iron determined in the usual manner (5).

The Evelyn 520 filter was then replaced by an Evelyn 420 M filter, and the sleeve rotated a quarter turn and lowered so that the upper aperture was opposite the light source. A tube containing 15 ml. of isoamyl alcohol was inserted, and the galvanometer deflection adjusted to give a reading of 100.0. The control tube was then replaced by the sample, and the reading of the galvanometer noted. The concentration of copper in the alcohol phase was determined from a previously prepared calibration curve (Fig. 2).

A study of this procedure confirmed McFarlane's (9) findings that the copper carbamate salt is quantitatively extracted by the isoamyl alcohol, and that the colour intensity then follows Beer's law. The latter point is well illustrated in Fig. 2, in which the concentration of copper, plotted against $2 - \log G$, is shown to be a straight line over the range 0-4.5 γ of copper per ml. Experiments on the recovery of copper and iron from mixtures of the

two have shown that 3.35 γ of added copper can be quantitatively recovered from a mixture containing 104 γ of iron, and that 7.35 γ of iron added to a solution containing 47.25 γ of copper can be quantitatively recovered. The method can be applied to solutions containing from 0.2–2.0 γ of iron and from 0.2–2.25 γ of copper per ml. For concentrations of iron greater than 2 γ per ml., the aqueous layer was diluted with a suitable volume of water before the iron determination was made and after the copper reading had been taken.

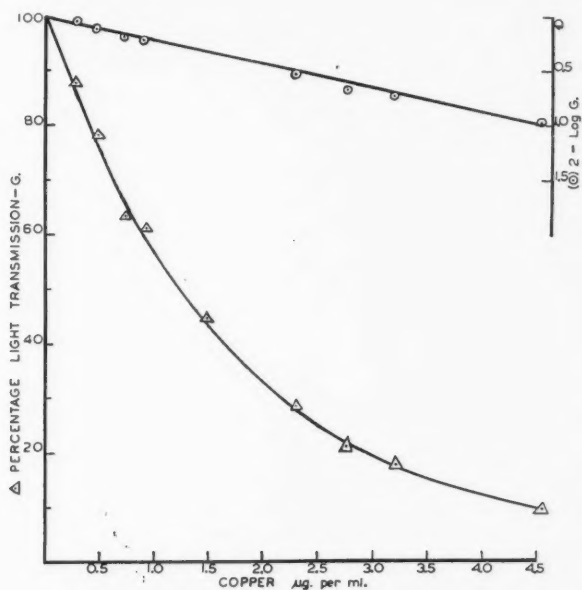


FIG. 2. Calibration curve and application of Beer's law.

The second procedure has also been used to determine the amount of free copper in Bordeaux sprays. It was found that the high concentration of calcium in the solution caused the golden-yellow colour of the copper carbamate to fade rapidly. This difficulty could be overcome by using a large excess of the carbamate reagent; the addition of 0.1 gm. of solid sodium diethyldithio carbamate to the final test solution gave a stable colour and reproducible results. It is possible that this difficulty may be experienced in the determination of copper in materials that contain a large amount of calcium.

Acknowledgments

The authors are indebted to Prof. W. D. McFarlane for his advice and criticism, and to Dr. J. A. Dauphinee, University of Toronto, for many helpful suggestions.

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THE SYSTEMS CHRYSENE-1 : 2-BENZANTHRACENE AND 1 : 2-BENZANTHRACENE-TRIPHENYLENE¹

BY M. G. STURROCK² AND T. LAWE³

Abstract

The liquidus-solidus curves of the systems chrysene-1 : 2-benzanthracene and 1 : 2-benzanthracene-triphenylene are given. They provide a convenient method for the evaluation of the percentage composition of these mixtures.

In the course of an investigation on the composition of high boiling coal tar oils by fractional distillation, one large fraction was found to be a prolific source of some lesser known coal tar hydrocarbons. In addition to chrysene, its isomers 1 : 2-benzanthracene and triphenylene were obtained in good yield. The liquidus-solidus curves provide a convenient method for the evaluation of the percentage composition of chrysene-1 : 2-benzanthracene and 1 : 2-benzanthracene-triphenylene mixtures. Chrysene-1 : 2-benzanthracene mixtures form a continuous series of solid solutions in which all freezing points lie between the freezing points of the pure components. 1 : 2-Benzanthracene-triphenylene mixtures form a discontinuous series of solid solutions in which the freezing point curve exhibits a eutectic point at 130° C. at 63% 1 : 2-benzanthracene.

The short range fraction boiling at 310° C. at 40 mm. pressure (440° C. at 760 mm.), obtained by fractionation of the crude heavy oil at 10 mm. pressure through an efficient column filled with Stedman wire gauze packing (10), was crystallized from benzol. The first product was chrysene. Subsequent crops of crystals obtained by evaporation of the chrysene mother liquor proved to be crude 1 : 2-benzanthracene. When no further crystals were obtainable, alcohol was substituted for benzol as the solvent. A mixture of 1 : 2-benzanthracene and triphenylene separated from the alcohol, from which pure triphenylene was easily prepared by further crystallization from the same solvent.

The chrysene was purified by crystallization from benzol after removal of the chrysogen by absorption from benzol on a tower of activated alumina; pale yellow lustrous plates showing blue fluorescence in daylight, m.p. 255° C. corr.; quinone, 239° C. corr.; complex with trinitrobenzene, 192 to 194° C. corr. The melting points given in the literature for chrysene and these derivatives are as follows:—melting point, 248 to 249° C. (4), 251 to 252° C. (6), 256° C. (11); the quinone, 239° C. (6); complex with trinitrobenzene, 194 to 195° C. (9). The 1 : 2-benzanthracene was brought to about 98% purity

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Contribution from The Research Laboratories, Dominion Tar & Chemical Company Limited, Montreal, Canada.

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by fractional crystallization from alcohol, at which point it was found convenient to complete the separation from chrysene by the formation of a maleic anhydride-1 : 2-benzanthracene adduct (3). The pure hydrocarbon was recovered from the adduct as colourless plates showing a faint blue fluorescence in daylight; m.p., 160° C. corr.; picrate, 142° C. corr.; styphnate, 152° C. corr.; quinone, 166° C. corr. The following values are given for 1 : 2-benzanthracene and these derivatives—m.p. 158.5 to 159.5° C. (4), 155 to 157° C. (6), 159° C. (2), 160.5° C. (5); picrate, 142 to 143° C. (6), 141.5 to

TABLE I
MELTING POINTS AND FREEZING POINTS OF THE SYSTEM CHRYSENE-1 : 2-BENZANTHRACENE

Chrysene, %	1 : 2 Benzanthracene, %	M.P., °C., corr.	F.P., °C., corr.
0	100	160	160
10	90	163	175
25	75	169	197
40	60	178	214
50	50	188	223
60	40	195	232
75	25	211	243
90	10	232	252
100	0	255	255

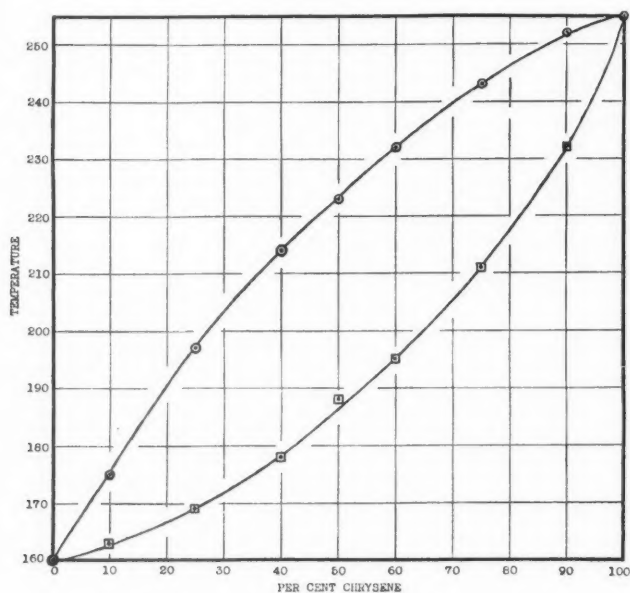


FIG. 1. Chrysene-1 : 2-benzanthracene liquidus-solidus curves.

142.5° C. (2); styphnate, 153° C. (2); quinone, 165 to 167° C. (6), 168° C. (2). The triphenylene, long colourless needles from alcohol, melted at 197° C. corr. The melting points given for triphenylene are 196° C. (8), 196.5° C. (7) and 198° C. (1).

The determinations were carried out on known mixtures of the pure components which were melted together, mixed, allowed to solidify and finely pulverized. The melting points and freezing points were obtained by determining the temperatures of incipient fusion and complete liquefaction by the capillary tube method, the temperature being raised very slowly and the material observed through a low power microscope.

TABLE II
MELTING POINTS AND FREEZING POINTS OF THE SYSTEM 1 : 2-BENZANTHRACENE-TRIPHENYLENE

1 : 2 Benzanthracene, %	Triphenylene, %	M.P., °C., corr.	F.P., °C., corr.
0.0	100.0	197	197
25.0	75.0	152	184
27.5	72.5	139	183
30.0	70.0	130	181
50.0	50.0	130	154
63.0	37.0	130	131
65.0	35.0	130	132
75.0	25.0	130	141
80.0	20.0	130	146
85.0	15.0	131	150
90.0	10.0	148	154
100.0	0.0	160	160

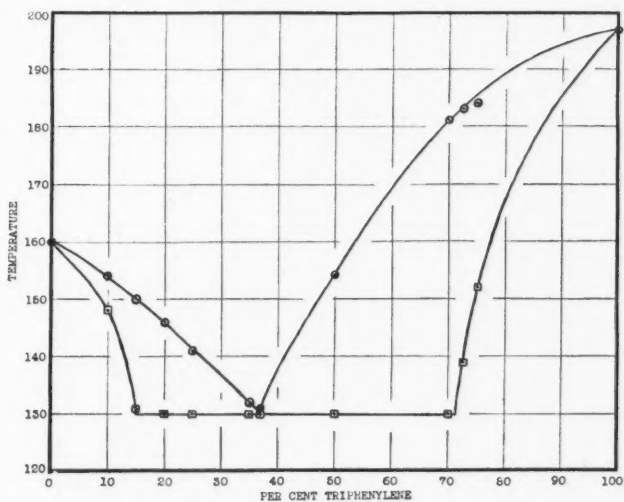


FIG. 2. 1 : 2-Benzanthracene-triphenylene liquidus-solidus curves.

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2,3-DIPHENYLBUTADIENE-1,3¹

BY C. F. H. ALLEN², C. G. ELIOT³ AND A. BELL⁴

Abstract

2,3-Diphenylbutadiene has been prepared and its behaviour in addition reactions investigated. It forms a 1,4-dibromide, a 1,4-monobromide by addition of one molecule of hydrogen bromide, is reducible to the saturated hydrocarbon, combines with oxides of nitrogen to form two isomeric dinitrobutenes, and couples with diazonium compounds. In the diene synthesis, products have been secured from maleic anhydride, acetylene dicarboxylic ester, quinone, and α -naphthoquinone. In so far as comparable reactions have been examined, 2,3-diphenylbutadiene resembles 2,3-dimethylbutadiene in the types of products formed by addition. Certain discrepancies recorded in the literature among related dibromides have been cleared up.

While investigating the action of acidic reagents on pinacols, Thörner and Zincke (21) heated acetophenone-pinacol (I) in a sealed tube with acetic anhydride and obtained a hydrocarbon, $C_{16}H_{14}$, which proved to be 2,3-diphenylbutadiene (II). Owing to the low yield and its ease of polymerization, it was not further studied. This work was repeated by Johlin (10) who found that the procedure gave erratic results, a ketone (III), formed by a pinacolone type of rearrangement of the diol, frequently being obtained; the melting points of the ketone and the diene were fairly close and the identity of the reaction products was not easily determined. Johlin reported, incorrectly, that the diene would not add bromine.

Stobbe (20, p. 300) treated the pinacol (I) with acetyl bromide, followed by phosphorus pentabromide and, with difficulty, obtained a dibromide, $C_{16}H_{14}Br_2$, which he thought was (IV) but which is shown below to be (VI). Obviously the reaction proceeds through the intermediate formation of the diene, which it has been found possible to obtain in a yield of 30% by working up the mixture produced by the acetyl bromide treatment. On account of its tendency to polymerize, the hydrocarbon is best kept in the form of its dibromide.

Beschke (3, pp. 120, 149) thought he had obtained this diphenylbutadiene, as a result of removing bromine from the dibromide (IV) with zinc; but, as will be shown below, his hydrocarbon was the *cis*-dimethylstilbene (V). Lévy (12, pp. 878, 890) prepared *trans*-2,3-diphenylbutene-2 (V) and a dibromide from it. Ott (15, p. 2135) secured what he considered to be the

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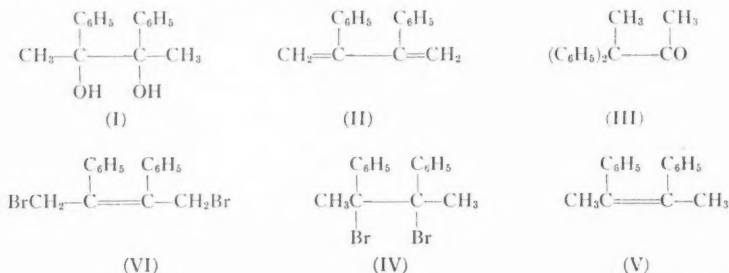
Presented at the Milwaukee Meeting of the American Chemical Society, September, 1938.

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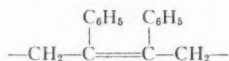
⁴ Research Chemist, Eastman Kodak Company.

cis-form of this hydrocarbon (V) and the isomeric 1-butene by controlled catalytic reduction of 2,3-diphenylbutadiene.



In this paper the preparation and reactions of 2,3-diphenylbutadiene are described, and the apparent confusion and uncertainties among the dibromides and related substances are cleared up. Preliminary studies showed that Johlin's procedure was unsatisfactory on account of the low yield and erratic behaviour. On the assumption that the amount of polymer might be decreased by the use of antioxidants, several of these were added to the contents of the sealed tube before heating; phenyl- β -naphthylamine proved to be the most useful. Instead of appreciably reducing polymerization, however, this prevented the rearrangement to the ketone, thus making it possible to secure the diene in each run. Even so, this procedure is less convenient than the reaction between the pinacol and acetyl bromide.

The polymer, on destructive distillation, gave acetophenone, dimethylstilbene, and a tar. This suggests that the structural unit is



Since the pure stilbene can be distilled without decomposition, the acetophenone may have come from one of the terminal groups of the polymer.

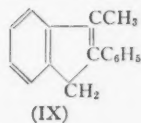
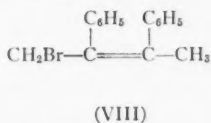
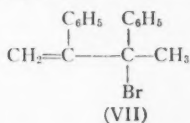
2,3-Diphenylbutadiene readily added one molecule of bromine in a variety of solvents to form a single dibromide. Upon ozonolysis of the dibromide, phenacyl bromide was formed; there was no evidence for any formaldehyde, which was especially looked for. This indicates that the dibromide is correctly represented by the structure (VI), and probably results from the 1,4-addition of bromine. As confirmatory evidence, may be mentioned the fact that it can be recrystallized without change from alcohol. An exact repetition of Stobbe's procedure gave this same dibromide. We suspect that Johlin's failure to secure a dibromide by addition may be attributed to the fact that he unknowingly had the ketone; the melting points of the diene and pinacolone are close, and the two substances are easily confused.

The isomeric dibromides (IV) were obtained by the addition of bromine to the *cis*- and *trans*-dimethylstilbenes (V). One form had been described previously by Lévy (12, pp. 878, 890); the other is new. Both isomers furnished the *cis*-stilbene on removal of the bromine by zinc. This latter

reaction thus serves to differentiate the dibromides (IV) and (VI), since the unsharp melting points, which lie in the same range, are accompanied by decomposition; even so, mixed melting points are depressed. The identification of the dibromides, therefore, involves the determination of melting points, removal of bromine by zinc, and determination of the melting points of the hydrocarbons, alone and on admixture. In this way it was shown that Beschke had correctly represented his dibromide as one form of (IV), but that the hydrocarbon, resulting from the action of zinc, was *cis*-dimethylstilbene, and not the diene (II) as he thought.

Ott has already described the products resulting from catalytic reduction of 2,3-diphenylbutadiene without details (15, p. 2135); these were to be included in a subsequent paper (that has not yet appeared). He stated that complete reduction gave a mixture of the saturated 2,3-diphenylbutanes, whereas with one equivalent of hydrogen, a mixture resulted, as mentioned above. The former result has been confirmed, but with the latter reaction considerable unchanged diene was recovered, while the residual oil had the characteristic odour of *d,l*-2,3-diphenylbutane. The diene was unaffected by 3% sodium amalgam; sodium in liquid ammonia gave the *meso*-butane and a trace of an unidentified hydrocarbon that did not decolorize bromine. The butanes were synthesized, for purposes of comparison, by a Wurtz reaction from α -bromoethylbenzene.

When a chloroform solution of 2,3-diphenylbutadiene was saturated with hydrogen bromide, a monobromide was obtained; this was also secured from the mixture furnished by the action of acetyl bromide on the pinacol (I). Hydrogen bromide was very easily removed by alcoholic or aqueous solutions, and it gave an immediate precipitate with silver nitrate. These reactions, and its preparation from the pinacol by means of acetyl bromide, would suggest Structure (VII), which could have been formed by a 1,2-addition of hydrogen bromide to the diene. However, ozonolysis of the substance furnished acetophenone and phenacyl bromide, but no detectable formaldehyde; hence it must be a 1,4-addition product as shown in (VIII). Con-

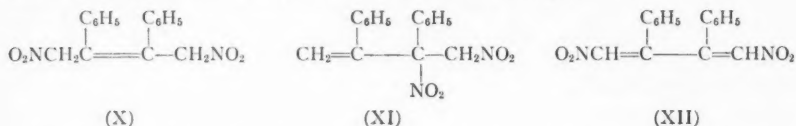


firmation of this structure was given by the production of the known (4) 3-methyl-2-phenylindene (IX) when the bromide reacted with zinc.

There is no evidence to indicate whether the bromide (VIII) is formed directly by addition at the ends of the conjugated system or by a rearrangement of an intermediate 1,2-addition product (VII). The mode of addition of hydrogen bromide to the diene did not seem to be appreciably affected by the presence of catalysts. The yield was the same when ascaridole or phenyl- β -naphthylamine was present, and but slightly less with thiophenol.

Wieland and Stenzl (25, 26) showed that 1,4-diphenylbutadiene added oxides of nitrogen in the 1 and 4 positions to give a dinitro derivative. This

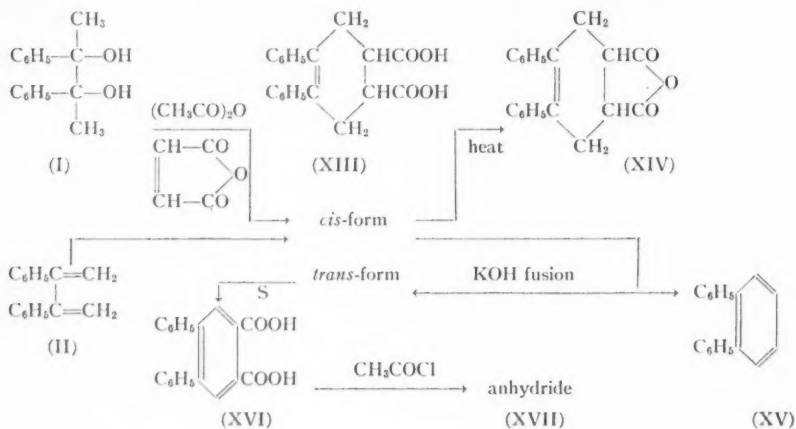
has been repeated and confirmed. 2,3-Diphenylbutadiene also added oxides of nitrogen and gave a pair of substances analyzing for the addition of 2 NO₂. The lower melting isomer formed a disodium derivative immediately, and hence must be one of the two possible 1,4-addition products (X). Upon permanganate oxidation, the higher melting form yielded benzil, while ozonolysis furnished formaldehyde; hence, it must have the structure (XI). It was slowly converted by sodium methylate into a disodium derivative that on acidification yielded the 1,4-addition product (X); this is equivalent to a rearrangement of the allylic type, and probably the first instance in which such a shift of a nitro group has been observed. Neither isomer was affected by hydrogen bromide. It appears, then, that both 1,2- and 1,4-additions have taken place with this diene and oxides of nitrogen.



When the sodium salt of the dinitro derivative was treated with bromine, a yellow substance was formed. Analysis showed that this substance differed from the starting material by two hydrogens. Since it was easily oxidized to form benzil, it is the dinitrodiene (XII).

2,3-Diphenylbutadiene coupled with diazotized 2,4-dinitroaniline and picramide, but the coloured products were unstable and could not be prepared analytically pure.

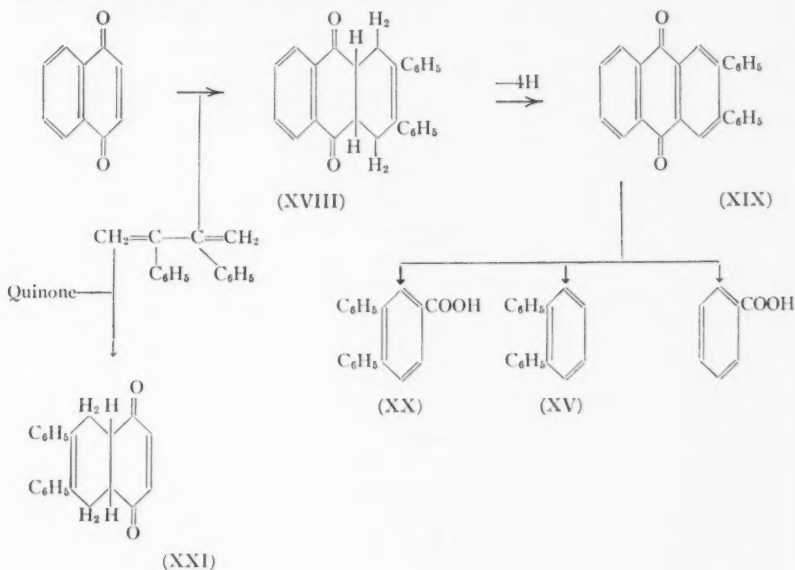
When examined with addends commonly employed in the diene synthesis, the diene was largely recovered unchanged; there seemed to be little tendency towards the formation of an addition product in most instances. The only useful second components proved to be maleic anhydride, quinone, and α -naphthoquinone. The series of reactions involving maleic anhydride and related substances is conveniently summarized by the flow sheet:—



The first reactions were carried out in a sealed tube under the best conditions for dehydrating the pinacol, with the hope that the maleic anhydride would add to the diene before it polymerized; this hope was not realized, most of the pinacol being rearranged and dehydrated to the pinacolone (III).

The *cis* form of diphenyltetrahydrophthalic acid (XIII) resulted from the addition reaction. On being heated above the melting point it lost water to give an anhydride (XIV). On fusion with potassium hydroxide, the *cis*-acid in part furnished the isomeric *trans* form, with some *o*-diphenylbenzene (XV), obviously a result of decarboxylation and dehydrogenation, and in part reversed into its components. The production of *o*-diphenylbenzene proved that a six-membered ring was formed in the addition reaction. When heated with sulphur, the acid was dehydrogenated to the aromatic diphenylphthalic acid (XVI); the anhydride of (XVI) was obtained on dehydration of the acid with acetyl chloride. On fusion with resorcinol and dehydrating agents, the anhydride gave a fluorescein-like melt which was brominated and iodinated—these reactions being only qualitatively studied since the colours were rather muddy.

2,3-Diphenylbutadiene reacted with α -naphthoquinone in boiling xylene to form the expected addition product (XVIII). This was easily dehydrogenated to 2,3-diphenylanthraquinone (XIX). Alkaline fusion of (XIX) gave the expected cleavage products, 3,4-diphenylbenzoic acid (XX), *o*-diphenylbenzene (XV), and benzoic acid.



Only one equivalent of the diene added to benzoquinone; the addition product (XXI) rapidly decolorized permanganate. The diene did not

appear to have reacted with acetylene, phenylacetylene, benzoylphenylacetylene, benzoylacrylic acid or sulphur dioxide.*

A comparison of 2,3- and 1,4-diphenylbutadienes is not strictly possible, since the latter is capable of geometrical isomerism, which may affect the ease and mode of addition. The most conspicuous differences are (i) the formation of a 1,4-dibromide with the 2,3-isomer, whereas the 1,4-analogue furnishes a 1,2-addition product, (ii) the addition of hydrogen bromide to the former, and (iii) the ease with which the 1,4-diene enters into the diene synthesis, a process obviously dependent on spatial configuration. In all the reactions that have been duplicated in both series, 2,3-diphenylbutadiene resembles 2,3-dimethylbutadiene.

Experimental

Of the two procedures investigated for securing the necessary acetophenone-pinacol, the one involving reduction in *i*-propanol solution in the sunlight (5, 16, p. 68) is preferred to the action of methylmagnesium iodide on benzil (10, 18, 22); the latter serves if time is an important factor. The mixed stereoisomers are dehydrated without separation. The diene did not crystallize readily from the oily mixtures that resulted in the various reactions, so it was usually detected and identified by formation of the dibromide (VI). In each instance where ambiguity was possible, the dibromide was treated with zinc, and the regenerated diene compared with an authentic specimen. The diene can be kept in the dark under nitrogen for several weeks, but otherwise it quickly becomes greasy and coloured.

2,3-Diphenylbutandiol-2,3 (I)

A one litre Pyrex flask containing a mixture of 90 gm. of acetophenone,† 850 cc. of *i*-propanol and one drop of acetic acid was inverted in sunlight for several months, the solvent removed *in vacuo*, and the residual oil allowed to stand; a 66% yield of the mixture (m.p. 83 to 114° C.) of pinacols slowly crystallized. It was recrystallized from a 5:1 mixture of benzene and petroleum ether (30 to 60° C.). The nature of the residual oil was not determined; it did not give carbonyl derivatives nor a solid dibromide, but evolved hydrogen bromide on treatment with bromine.

2,3-Diphenylbutadiene (II)

To 35 gm. of acetophenone-pinacol containing a trace (0.02 ± gm.) of phenyl-β-naphthylamine, in a brominating flask, was slowly added 105 cc. of acetyl bromide. When the vigorous reaction was over, the excess halide was removed under reduced pressure and the cooled residue cautiously neutralized with aqueous sodium carbonate. The insoluble, oily precipitate (m.p. 69 to 73° C.) was filtered and dissolved in hot alcohol; on dilution to incipient cloudiness and cooling, a 30% yield of the diene (m.p. 45 to 47° C.) separated. Instead of isolating this crude product, it is preferable to take it up in chloro-

* Backer (2) described a sulphone, formed in a yield of 90% by heating the diene and sulphur dioxide in a sealed tube.

† A generous supply of this ketone was donated by Compagnie Parento, Limited.

form, dry the solution with calcium chloride, and convert it into the dibromide by addition of a chloroform solution of bromine. After evaporation of the solvent, a hexane wash left 17.7 gm. (33.5%) of dibromide, m.p. 144 to 147° C.

To secure the diene from the dibromide, to 15 gm. of the latter in 50 cc. of acetone was gradually added 7 gm. of zinc dust; when the vigorous action had subsided, the whole was refluxed for two hours, filtered hot, and evaporated to dryness. The residue was taken up in hot alcohol and water added to incipient cloudiness; on chilling in a freezing mixture, 7.8 gm. (92%) of the diene, m.p. 46 to 47° C., was obtained. Acetyl chloride was without effect (cf. ref. 21).

Johlin's sealed tube procedure (10) also gave a 30% yield of the diene if phenyl- β -naphthylamine or copper acetate was added to the reaction mixture; a considerable quantity of polymer resulted in every run. In the absence of these added antioxidants the yields were erratic, mostly the pinacolone (III), resulting by rearrangement of the glycol, being obtained; after analysis it was identified by its melting point and the melting point of its oxime, 151° C. (18). The diene from these runs melted at 47 to 48° C.

The polymer, left behind in the steam distillation, gradually hardened to a dark wax, softening at about 40° C. On vacuum distillation of the soft polymer it gave half its weight of a liquid (b.p. 140 to 170° C. at 20 mm.) from which were separated a little acetophenone (2,4-dinitrophenylhydrazone, m.p. 233 to 234° C.) and an oil which with bromine formed a dibromide (IV) identical with that obtained from *trans*-dimethylstilbene. The oil, thus, contains dimethylstilbene.

When maleic anhydride in acetic anhydride was used as the dehydrating agent, a trace of the addition product and a little of the acid (XIII) were isolated, but most of the diol rearranged to the pinacolone; maleic anhydride alone had no effect. The mixed anhydrides at room temperature, after four months, gave a 20% yield of the acid. Chloroacetic anhydride gave only the pinacolone.

Addition Reactions of 2,3-Diphenylbutadiene

(a) The Bromides

(1) *Addition of Bromine; 2,3-Diphenyl-1,4-dibromobutene-2 (VI).* A chloroform solution of 2,3-diphenylbutadiene was treated with bromine in chloroform until the colour persisted after shaking; heat was evolved and towards the end of the addition hydrogen bromide was evolved. The solvent was evaporated, and the residue was recrystallized from acetone. It formed long prisms, m.p. 145 to 147° C. with decomposition. It could be recrystallized from dilute alcohol without appreciable decomposition. Calcd. for $C_{16}H_{14}Br_2$: C, 52.5; H, 3.9; Br, 43.7%. Found: C, 52.5; H, 3.8; Br, 43.9%. The same dibromide was secured by following Stobbe's procedure exactly (20, p. 300).

When dissolved in acetone and refluxed with an excess of zinc dust for two hours, the diene separated practically quantitatively from the filtered solution.

It slowly gave a precipitate of silver bromide with hot alcoholic silver nitrate. It very slowly decolorized permanganate in acetone, and very slowly liberated iodine from an acetic acid solution of potassium iodide. It was unaffected by distilling a solution in acetyl bromide.

Ozonolysis. A carbon tetrachloride solution of 2 gm. of the dibromide was ozonized at 0° C. for three hours. On decomposition by water 0.2 gm. of a lachrymatory solid resulted, which was shown to be phenacyl bromide. No constituent of the remaining oil could be identified; attempts to determine the presence of formaldehyde were all negative (7, 14, 24).

(2) *Addition of Hydrogen Bromide; 2,3-Diphenyl-4-bromobutene-3 (VIII).* A solution of 2 gm. of the diene in 20 cc. of chloroform, to which a drop of ascaridole had been added, was saturated with hydrogen bromide. The mixed oil and solid that remained after removal of the solvent was triturated with hexane to remove the oil; this treatment yielded white prisms of the monobromide. After two recrystallizations from hexane, the product remained stable for several months, but otherwise soon became oily. The pure substance melted at 78° C. Calcd. for $C_{16}H_{15}Br$: Br, 27.8%. Found: Br, 27.5, 27.9%. The yield was 72% in the presence of phenyl- β -naphthylamine, 73% with ascaridole, and 62% with thiophenol. The oil which remained in the hexane was largely unchanged diene. A large-sized run (11 gm. of diene) gave 73% of monobromide, and 15% of the diene (recovered as dibromide). The residual oil almost entirely decomposed on attempted vacuum distillation. This same bromide was also easily isolated from the greasy solid left after the acetyl bromide treatment of the diol, by triturating with petroleum ether (90 to 100° C.).

Ozonolysis* gave only phenacyl bromide (mixed m.p.) and acetophenone (2,4-dinitrophenylhydrazone, mixed m.p.) but no trace of formaldehyde (9, p. 743). The bromobutene gave instantly a quantitative precipitate of silver bromide with alcoholic silver nitrate. A hot alcoholic solution deposited the diene on cooling.

3-Methyl-2-phenylindene (IX). Four grams of zinc dust was added, as fast as the violence of the reaction permitted, to 6 gm. of the bromobutene in 50 cc. of acetone, and, after refluxing for one hour, the solvent was evaporated. The crystals that separated from the residual oil were filtered and washed with acetone; the yield was 0.12 gm. (2.8%), m.p. 210° C. Calcd. for $C_{32}H_{30}$: C, 92.7; H, 7.3%; mol. wt., 414. Found: C, 92.9; H, 7.5%; mol. wt. (Rast) 384, 376. Two possibilities are a diindene and 2,3,6,7-tetraphenyl-octadiene-2,6. The quantity was too small to be significant and it was not further studied. It showed a strong violet fluorescence, which favours a condensed ring formula rather than an open chain isomer.

Since the oil still contained halogen it was refluxed with more zinc an additional three hours and distilled *in vacuo*; b.p. 130° C. at 7 mm. This oil was largely the indene; the latter separated in needles from alcohol, m.p. 75 to

* For ozonolysis of the bromo and dinitrobutenes we are greatly indebted to Dr. G. F. Wright and Mr. A. J. Benson of the University of Toronto.

76° C. (4). Calcd. for $C_{16}H_{14}$: C, 93.1; H, 6.9%. Found: C, 92.5; H, 6.8%. The oil contained a little diphenylbutadiene, separated and identified as the dibromide; about one gram of residue remained in the distilling flask.

(b) Reduction

The use of Adams' platinum oxide catalyst (1) gave an oil, from which a 55% yield of the solid *meso*-2,3-diphenylbutane separated. The pleasant-smelling residual oil was probably a mixture of the two isomers, since the difficultly separable *d,l*-form is reported to melt at 8° C. and have a strong odour. Stepwise reduction was not fully investigated, owing to Ott's partially completed work (15, p.2135).

Seventy-five hundredths of a gram of the diene, 0.2 gm. of catalyst, and 70 cc. of alcohol were shaken for 2.5 hr., the catalyst was filtered, and the solvent allowed to evaporate. The crystals were purified (Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6%. Found: C, 91.5; H, 8.1%.) and found to be identical with the same hydrocarbon secured by a Wurtz reaction from α -bromoethylbenzene (below). With one equivalent of hydrogen, 0.3 gm. of the diene (0.7 gm. used) was recovered unchanged, the remainder being an anise-smelling oil that still decolorized bromine.

An alcoholic solution of the diene was unattacked by 3% sodium amalgam after five hours' refluxing, but was reduced by sodium in liquid ammonia. To a mixture of 0.3 gm. of the diene, 40 cc. of ether, and 30 cc. of ammonia was added, very slowly, 0.5 gm. of sodium in 30 cc. of ammonia; the deep blue colour decreased gradually. The solvent was removed at room temperature, with intermittent stirring—the blue colour suddenly disappeared, leaving a whitish sludge in a pale green solution. After complete evaporation, the residual jelly was boiled with alcohol saturated with carbon dioxide, filtered, and the filtrate evaporated to dryness. It was boiled with methanol, again carbonated and filtered, and evaporated to about 30 cc. The saturated hydrocarbon (VII) (high melting isomer) was filtered; further evaporation gave a second crop. The total yield was 55%. The residual oil had the same odour as mentioned above. In one instance the first crystals that separated in a very small amount were recrystallized from acetone, forming needles, m.p. 169° C. They did not decolorize bromine, and are thought to be a bimolecular reduction product (Calcd. for $C_{32}H_{34}$: C, 91.9; H, 8.2%. Found: C, 91.9; H, 8.4%).

Synthesis. The α -bromoethylbenzene was obtained by saturating 50 gm. of phenylmethylcarbonyl acetate* in 125 cc. of acetic acid with hydrogen bromide; after 48 hr., the solution was poured into 750 cc. of water, the oil that separated being removed, washed with sodium bicarbonate solution, and dried over calcium chloride. On distillation *in vacuo*, 42.2 gm. (75%) came over at 105 to 108° C. at 28 mm. It was then mixed with acetone and zinc dust added; after the vigorous reaction was over, the filtered solution was evaporated to crystallization. The solid *meso*-diphenylbutane separated from the anise-smelling oil; it was recrystallized until odourless; m.p. 122° C.

* We are very grateful to the Compagnie Parento, Limited, for a generous supply of this ester.

(c) Addition of Nitrogen Dioxide

2,3-Diphenyl-1,4-dinitrobutene-2 (X) and 2,3-Diphenyl-3,4-dinitrobutene-1 (XI). The gases produced by heating 40 gm. of lead nitrate were absorbed in 100 cc. of chilled hexane. This was added to a chilled solution of 6.5 gm. of diphenylbutadiene in 100 cc. of hexane; 7.5 gm. (80%) of a pale yellow solid separated. This was filtered, washed, and dried (m.p. 116 to 145° C.). It was shaken with 25 cc. of methanol, which left 3.3 gm. (35%) residue that on recrystallization from hot methanol furnished white rods, m.p. 192° C. (XI). The soluble portion was fractionally crystallized into nearly equal parts of the same substance (XI) and its isomer (X); the latter formed white needles, m.p. 151° C. Calcd. for $C_{16}H_{14}O_4N_2$: C, 64.4; H, 4.7; N, 9.4%. Found: (XI) N, 9.2; (X) C, 65.0; H, 4.8; N, 9.3%.

The high melting isomer crystallized well from benzene or chloroform, but methanol was preferred for purification. A mixture of both isomers was often encountered; it separated from dilute alcohol, with a melting point of 138° C. \pm and was temporarily mistaken for a third isomer.

The high melting isomer (0.5 gm.) dissolved in 10 cc. of concentrated sodium methylate to give an orange solution; when this was added to acetic acid and diluted, the isomeric dinitrobutene (X) was precipitated. When the latter was treated in a similar manner, a yellow crystalline disodium salt separated. On acidification with acetic acid, the starting material was regenerated. Calcd. for $C_{16}H_{12}N_2O_4Na_2 \cdot CH_3OH$: Na, 12.3%. Found: Na, 11.8, 12.0%.

Ozonolysis. This took place very slowly; from 0.2 gm. of substance (XI) in chloroform, 0.16 gm. was recovered unchanged. The aqueous layer from the decomposition was treated with dimedon, and 12 mg. (45% of theory) of the derivative of formaldehyde was obtained (9, p. 743) and identified in the usual way.

Oxidation. A mixture of 0.3 gm. of the dinitrobutene (XI), 2 gm. of potassium permanganate and 50 cc. of water was heated in a distilling flask, and the solid that steam distilled was collected and identified as benzil; there was no depression on admixture with an authentic specimen.

2,3-Diphenyl-1,4-dinitrobutadiene (XII). When the chilled solution of the disodium salt was diluted sufficiently to keep it all in solution, and bromine added dropwise until the colour persisted, a yellow solid separated. This was recrystallized from hot methanol, from which it separated in yellow rods, m.p. 184° C. with decomposition. Calcd. for $C_{16}H_{12}O_4N_2$: C, 64.9; H, 4.1; N, 9.5%. Found: C, 65.3; H, 4.2; N, 9.4%.

This was readily oxidized by potassium permanganate in hot acetone solution; the oxides of manganese were filtered and the residue, after evaporation of the solvent, boiled with alcohol and filtered hot from unoxidized starting material. On cooling, the alcohol deposited benzil, identified in the usual manner.

A preliminary repetition of Wieland's addition of nitrogen dioxide to 1,4-diphenylbutadiene gave the 1,4-dinitrobutene with the properties described (25, 26).

(d) *Coupling*

To a mechanically stirred clear solution of 30 cc. of concentrated sulphuric acid, 10.5 cc. of water and 3 gm. of sodium nitrite (added to acid in two equal portions) below 10° C. was added dropwise 1.8 gm. of 2,4-dinitroaniline in 15 cc. of pyridine; after two hours, 1 gm. of sulphamic acid was introduced, followed by 2 gm. of 2,3-diphenylbutadiene in 15 cc. of pyridine (6, 13). The solution became red. After a few minutes, ice was added and finally considerable water; 1.65 gm. of unchanged diene separated and was recovered. The dye was extracted from the filtrate with chloroform, and precipitated by addition of petroleum ether (90 to 100° C.). The dark red solid had an unsatisfactory melting point (166 to 168° C.; decomposition at 230° ±) and could not be recrystallized. The yield was 0.35 gm., 55%. Calcd. for $C_{22}H_{16}O_4N_4$: N, 14.0%. Found: N, 12.1%.

In a similar fashion, but without pyridine (19), the diene dissolved in glacial acetic acid was coupled with diazotized picramide. A dull yellow solid was precipitated from the greenish solution and extracted with chloroform; it did not melt below 360° C., and charred on further heating.

(e) *The Diene Synthesis*

(1) *cis*-4,5-Diphenyltetrahydrophthalic acid (XIII). After refluxing 9 gm. of the diene, 5.5 gm. of maleic anhydride, and 100 cc. of benzene overnight, the acidic portion was extracted from any unreacted hydrocarbon with aqueous sodium hydroxide. On adding the latter to concentrated hydrochloric acid, 12.5 gm. (94%) of an ether-soluble acid was precipitated, which, after several recrystallizations from dilute alcohol or dilute acetic acid, melted at 193° C. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6%. Found: C, 74.9; H, 5.8%. Calcd. for $C_{20}H_{16}O_4Ag_2$: Ag, 40.3%. Found: Ag, 40.4%. This acid is quite soluble in the usual organic solvents except petroleum fractions.

This acid was also obtained in a 20% yield by allowing a mixture of 6 gm. of the pinacol, 11 gm. of maleic anhydride, and 16 cc. of acetic anhydride to stand at room temperature for four months. The anhydride of this acid was obtained in an impure state on long standing of the diene and maleic anhydride in xylene, from the acid by refluxing with acetyl chloride, or, preferably, by heating the acid just above its melting point as long as water was evolved; after recrystallization from benzene-hexane mixture it melted at 164° C. On fusion with resorcinol and a dehydrating agent, a fluorescent solution was obtained; the dye was brominated to give a dull red-brown dye. Calcd. for $C_{20}H_{16}O_3$: C, 78.9; H, 5.3%. Found: C, 79.2; H, 5.3%.

(2) *trans*-4,5-Diphenyltetrahydrophthalic acid (XIII). When the *cis* acid was fused with potassium hydroxide at 310° C. as long as gas was evolved, the melt dissolved in water, and the solution extracted with benzene, the *trans* isomer was isolated after acidification. It separated from dilute methanol or

acetic acid in needles, m.p. 228° C. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6%. Found: C, 74.4, 74.6; H, 5.6, 5.7%.

The benzene extract, mentioned above, was evaporated and the residue treated with methyl alcohol; *o*-diphenylbenzene was obtained—a mixed melting point with an authentic specimen was not depressed.

(3) *3,4-Diphenylphthalic Acid (XVI)*. A mixture of 3.4 gm. of the tetrahydro acid and 2 gm. of sulphur was melted at 200° C. for 16 hr. in a current of nitrogen; the evolved hydrogen sulphide was collected in aqueous silver nitrate, 3 gm. (30%) of silver sulphide being obtained. The cooled melt was extracted with aqueous sodium carbonate, the extract decolorized by Norit, and acidified with dilute sulphuric acid. The acid, 0.9 gm. (27%) recrystallized from methanol or benzene in rods, m.p. 205 to 206° C. with gas evolution. Calcd. for $C_{20}H_{14}O_4$: C, 75.5; H, 4.4%. Found: C, 75.4; H, 4.5%.

When boiled for a few minutes with acetyl chloride it furnished the corresponding anhydride, which formed prisms when recrystallized from benzene-hexane, m.p. 102° C. Calcd. for $C_{20}H_{12}O_3$: C, 80.0; H, 4.0%. Found: C, 79.6; H, 4.0%.

The same acid (XVI) was secured in small amounts by heating a mixture of the diene and acetylene dicarboxylic ester at 180 to 190° C. until it was a deep brown, extracting with alkali and acidifying the alkaline solution, and also from 3,4-diphenylfuran and maleic anhydride by the usual procedure of saturating an acetic acid solution of the addition product with hydrogen bromide (23).

(4) *2,3-Diphenylanthraquinone (XIX) and related substances*. A solution of 6 gm. of α -naphthoquinone and 8 gm. of 2,3-diphenylbutadiene in 100 cc. of xylene was refluxed for 2.5 hr. and left overnight. The solution was filtered from a trace of brownish sludge and the solvent removed *in vacuo*. The residue was recrystallized from 50 cc. of acetone; this afforded 10.4 gm. of a white addition product (XVIII), which was recrystallized from methanol. It formed needles, m.p. 175 to 176° C. Calcd. for $C_{26}H_{20}O_2$: C, 85.8; H, 5.5%. Found: C, 85.6; H, 5.7%.

This substance gave a red solution with alcoholic potash; when air was bubbled through, the 2,3-diphenylanthraquinone (XIX) slowly separated in a yield of 90%. It crystallized from acetic acid in yellow needles, m.p. 211 to 212° C. Calcd. for $C_{26}H_{16}O_2$: C, 86.7; H, 4.4%. Found: C, 87.1; H, 4.4%.

This quinone dissolved to a brown solution in concd. sulphuric acid from which it was recovered unchanged on dilution. In very dilute methyl alcohol, sodium hydrosulphite gave a green colour; addition of sodium perborate or acid regenerated the quinone. A red colour was produced by the use of zinc and sodium hydroxide; acidification changed the colour to yellow, and aeration for several hours regenerated the quinone.

Alkaline Fusion; 3,4-Diphenylbenzoic Acid (XX). A mixture of 0.9 gm. of the quinone and 2 gm. of moist potassium hydroxide was heated in a distil-

ling flask at 250° C. for four hours. After the addition of 50 cc. of water, the solution was distilled; ether extraction of the distillate gave 0.045 gm. (16%) of *o*-diphenylbenzene, identified in the usual manner.

On acidification of the residual solution, a white acid was precipitated; after solution in acetic acid and decolorizing, water was added to incipient cloudiness. 3,4-Diphenylbenzoic acid separated; a second crop was obtained by further dilution. The total amounted to 0.47 gm. or 69%. It was recrystallized from acetic acid, from which it separated in prisms, m.p. 218° C. Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1%. Found: C, 83.2; H, 5.3%. It recrystallized unchanged from acetyl chloride.

The original aqueous solution from the acidification was extracted with ether, and 0.15 gm. of benzoic acid obtained. A larger sized fusion gave 70% of (XX), 72% of benzoic acid, and 21% of *o*-diphenylbenzene.

(5) *Other Addends to Diphenylbutadiene.* Tetrahydrodiphenylnaphthoquinone (XXI) was obtained by heating 4 gm. of the hydrocarbon and 1.5 gm. of quinone in 20 cc. of benzene on the steam bath for 18 hr., and extracting unreacted diene with hexane from the residue after removal of solvent. The portion insoluble in hexane (1.6 gm.) was recrystallized from methanol, from which it separated in large pale yellow needles or rods, m.p. 163° C. Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.8%. Found: C, 84.4; H, 5.7%.

There was no detectable addition of acetylene, β -benzoylacrylic acid, phenylacetylene, benzoylphenylacetylene or sulphur dioxide.

(f) *The Bromination of the Dimethylstilbenes*

2,3-Diphenyl-2,3-dibromobutanes (IV). The *cis* and *trans* forms of dimethylstilbene were brominated in chloroform using 1 gm. of the hydrocarbon, 1.6 gm. of bromine, and 20 cc. of chloroform. The *trans* form gave 1.2 gm. of a dibromide that separated from hexane in needles, m.p. 149 to 152° C. When mixed with the dibromide (VI) from the diene, the melting point was depressed 10° C. The *cis* form gave a product that separated in diamond-shaped prisms, m.p. 142 to 144° C. with decomposition; mixtures with the dibromide from the *trans* form were depressed 10° C.

Both dibromides were unstable in alcoholic solutions, in contrast to the 1,4-dibromide (VI), giving oils. On refluxing in acetone solution with zinc dust for one-half hour, filtering, and concentrating to crystallization, both dibromides gave *cis*-dimethylstilbene, as shown by comparison with authentic specimens.

Beschke's dibromide was secured by following his procedure (3, pp. 120, 149), starting with *trans*-2,3-diphenylbutene-1,4-dicarboxylic acid.* A mixed melting point with the above dibromide from the *trans*-dimethylstilbene was not depressed, while that with the 1,4-dibromide from the diene was lowered 5° C.

* We are indebted to Mr. H. B. Yuen for the preparation of this substance.

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